Journal

American Leather Chemists Association

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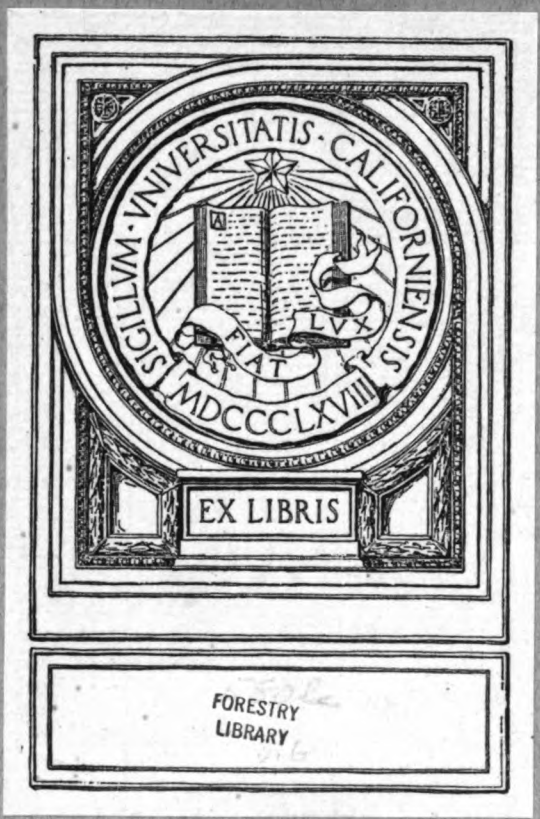

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The Journal of the American Leather Chemists Association

VOLUME VI, 1911

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS
ASSOCIATION

THE CHEMICAL PUBLISHING CO., PRINTERS
EASTON, PA.

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The Journal of the

American Leather Chemists Association

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Journal of the

American Leather Chemists Association

Vol. VI JANUARY, 1911 No. 1

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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COUNCIL MEETING.

A meeting of the Council was held at New York, December 3, 1910. The following members were present, Messrs. Russell, Reed, Teas, Hoppenstedt, Griffith and Alsop.

The National Tanners Association desiring that two members serve on their Advisory Committee for the tanners institute. J. H Russell and J. H. Yocum were appointed in accordance with their suggestion.

The Secretary was requested to send out a form to the active members and endeavor to secure from them information that would be of use in making up committees and lead to better support of this important part of the Association's work.

The following committees have not presented reports as yet.

On the Detection of Tanning Materials in Mixtures, A. L. Dean, Chairman.

On the Cure and Disinfection of Hides, V. A. Wallin, Chairman.

"Chrome" Committee, S. S. Sadtler, Chairman.

The following subjects were chosen for committee work.

Analysis of Leather, F. P. Veitch, Chairman.

Acidity of Tanning Liquors, W. K. Alsop, Chairman.

Rapid Cooling of Tannin Solutions for Analysis, H. C. Reed, Chairman.

Disposition of Tannery Waste, J. H. Russell, Chairman.

Analysis and Detection of Sulphite Cellulose Extracts, P. H. Small, Chairman.

Plumping Effect of Acids, Lloyd Balderston, Chairman.

Oil Analysis.

Analysis of Extracts—C. W. Morris was appointed to secure collaborative analyses from the active members of three samples of extract, one chestnut, one unclarified quebracho and the other one to be selected by him.

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PROPOSED CHANGES IN METHODS.

At a meeting of the Council held December 3, 1910, the following proposed changes in methods were submitted in writing. In accordance with the By-Laws these are published in this issue of the JOURNAL.

Official Method for Tannin Analysis, Analysis of Extracts, Section 9, *Non-Tannins.* Third line commencing with "Digest" to read "ten times" instead of "twenty-five times." (This refers to the proportion of water to hide powder.)

Official Method for Tannin Analysis, Crude Materials. To Section 4, *Extraction of Sample,* shall be added the following:—4(a) *Fresh Materials; Woods and Barks, Also Spent Materials.* 500 cc. of extractive solution shall be collected by outside condensation in approximately two hours, and the extraction continued with 500 cc. for fourteen hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give by condensation, approximately 500 cc. in one and one-half hours.

Official Method for Tannin Analysis, Crude Materials, Section 4, *Extraction of Sample.* Fifth line commencing with "At least" to be altered to read "500 cc. etc."

METHODS OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR 1911.

OFFICIAL METHOD FOR TANNIN ANALYSIS.

I. Crude Materials.

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of Sample for Extraction*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of

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water for extraction should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatine salt solution fails to give a precipitate. At least 400 cc. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

(4A) *Sumac and Kindred Materials*:

Put the material (the amount should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water and allow to soak one hour. Then extract by collecting 2,000 cc. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand over night and analyze the following day by the Official Method for Extracts.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Method for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts.

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35-0.45 gram tannin per 100 cc. of

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solution. Dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir and pour on a 590 S. & S. 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

(9) *Non-Tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand overnight. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary; so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the original solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the filtrate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning until clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE.—In order to limit the amount of dried hide powder

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used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 per cent. to 75 per cent. water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatine 10 per cent. salt solution.

(10) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

III. Analysis of Liquors.

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-Tannins*:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide-powder shown in the following table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
0.35——0.45 gram	9—— 11 grams
0.25——0.35 gram	6.5—— 9 grams
0.15——0.25 gram	4——6.5 grams
0.00——0.15 gram	0—— 4 grams

Solutions to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

IV. Evaporation and Drying.

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer,"

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at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor greater than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(17) *Reagents*:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter, is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS.

General:—

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture, it is apparent that the sampling in all its details

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should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air-tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of the liquor which have set around with no preservative in them for some time do not represent the condition of the liquor when sampled.

(1) *Number of Packages to be Sampled*:

When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to sampled, 1 per cent. of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10 per cent. of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9 per cent. of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8 per cent. of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7 per cent. of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6 per cent. of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5 per cent. of the number of barrels shall be sampled. When from 421 to 500 barrels are to be sampled, 4 per cent. of the number of barrels shall be sampled. When more than 500 barrels are to be sampled 3 per cent. of the number of barrels shall be sampled.

(2) *Liquid Extract in Barrels*:

The heads shall be removed from the number of barrels

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specified in (1), the contents of each barrel stirred until homogeneous, and a sample of equal size taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples shall be drawn for analysis. These samples shall be preserved in air-tight glass containers, labeled with the date of sampling and such distinguishing marks as may be necessary. When a considerable period of time is likely to elapse between the sampling and the analysis, each individual sample shall be weighed when prepared and the certified weight of the sample be marked on the label.

(3) *Liquid Extract in Bulk*:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) *Liquid Extract in Tank Cars*:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE: As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge 3 minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container so soon as taken, be thoroughly mixed and sampled as in (2).

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(5) *Solid Extracts*:

The number of packages specified in (1) shall be selected, as nearly as practicable, of equal size. Whenever possible every n^{th} package shall be set aside for sampling while the extract is being unloaded. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up till it will pass through a sieve of 1 inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of the required size shall be taken, be wrapped in paraffine paper, and be enclosed in the smallest clean dry air-tight glass receptacles that will hold them, labeled, etc., as in (2).

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least two pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(6) *Crude Tanning Materials*:

A. Shipments in bags, mats, barrels or other similar packages.

The number of packages specified in (1) shall be emptied in uniform horizontal layers in a pile on some clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than two quarts each shall be preserved in air-tight containers properly labeled.

When the number of packages to be sampled is so great as to make one pile impracticable, two or more piles may be made, and the samples from the several piles properly mixed.

B. Shipments in bulk.

1. Nuts, Beans, Pods, Ground Materials, etc.

Equal portions shall be taken from at least ten uniformly

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distributed parts of the bulk, be mixed and sampled as in "A."

2. Bark, Wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least one quart in size be preserved in air-tight containers, as in "A."

(7) *Spent Material from Leaches*:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(8) *Tanning Liquors*:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint be taken for analysis. The addition of 0.03 per cent. of thymol of other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than one pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

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OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) *Preparation of Sample*:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) *Moisture*:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats*:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) *Ash*:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material*:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose*:

To 500 cc. of the solution obtained by extraction according to (5), add 20 cc. of normal lead acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry Na_2CO_3 and filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry Na_2CO_3 until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than 0.25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with

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water to 145 cc. if necessary, cover with a watch-glass, bring to boil and set in a boiling water-bath for exactly 30 minutes. Filter through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol, dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by 0.8883 and calculate to glucose according to the following table: (Published this JOURNAL, May, 1909, page 125, et seq. from J. S. C. I., **13**, 1227 et seq.)

(7) *Nitrogen*:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107, (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling-point of the acid

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from 5 to 15 minutes, or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHOD FOR COLOR VALUATION OF TANNING MATERIALS.

Immerse a piece of thoroughly wetted white broadcloth, three inches by four in size, in a solution of the material to be tested, containing 3 per cent. of tannin, and allow to remain with frequent agitation for 45 minutes. The solution previous to immersing the cloth is heated on a water-bath to 50° C. and the heat then turned off, the coloring being effected without a continuance of the heat. (Care must be taken that the temperature of the bath is not greater than that of the solution, *i. e.*, 50° C.) The solution, in volume 250 cc. should be contained in a porcelain or glass beaker not less than 3½ in. in diameter and 4 in. deep, and the beaker immersed at least 2½ in. in the water. The bath should not be exposed to rapid cooling (5° being the usual drop) during the test. At the expiration of the time of immersion, the cloth is removed from the solution and the free coloring matter washed out thoroughly in water heated to 50° C., then well squeezed in the hand and further excess moisture removed by rolling for a minute or two in a clean towel. It is then dried smooth between pieces of blotting paper in a letter press.

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PROVISIONAL METHODS FOR THE ANALYSIS OF OILS AND FATS.

Saponification Value.

Preparation of the Alcoholic KOH.—Purify the alcohol as follows: To ordinary alcohol add potassium permanganate in very fine powder or saturated solution until the pink color holds for about ten minutes; allow to stand over night, filter and distil over a fixed oil and sodium hydroxide, the first portions of the distillate, about a quarter, being rejected. Dissolve the KOH in the alcohol thus prepared, filter, and make up to half normal strength.

Determination.—Weigh off accurately in a flask holding 150-200 cc., 1.5-2.0 grams of the fat, or oil, purified and filtered if necessary. Next run into the flask 25 cc. of the alcoholic potash, attach a long cooling tube or invert condenser, and heat on the water-bath for thirty minutes, frequently imparting a rotary motion to the contents of the flask until complete solution has been effected, which can always be done unless there is considerable unsaponifiable material present. After this allow to simmer, but not to boil vigorously, for the remainder of the time. Next add 1 cc. of a 1 per cent. phenolphthalein solution prepared by dissolving 1 gram phenolphthalein in 100 cc. 90 per cent. alcohol and titrate back the excess of potash with half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, the same influence on the final result, and is thus eliminated. The difference in the number of cubic centimeters of acid used for the blank test and the real test corresponds to the quantity of potash required, and is calculated to milligrams of potash to 1 gram of fat.

Acid Value.

Weigh accurately a convenient quantity of the material to be tested into an Erlenmeyer flask, and treat with about 25 cc. of a mixture of alcohol and ether, previously rendered slightly pink with alcoholic KOH after the addition of 1 cc. 1 per cent. phenolphthalein solution. Then titrate the mixture to the same point to which the solvent had been brought. Use tenth-normal alcoholic KOH for this and from the number of cubic cen-

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timeters required, calculate the amount of KOH absorbed. This expressed as the number of milligrams per gram of substance is the acid value.

Iodine Value.

A. O. A. C. Official Method—The Hanus Method. Bulletin No. 107.

(*a*) *Preparation of Reagents—Hanus Iodine Solution.*—Dissolve 13.2 grams of iodine in 1,000 cc. of glacial acetic acid (99.5 per cent.) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration—3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal Sodium Thiosulphate Solution.—Dissolve 24.8 grams of chemically pure thiosulphate, freshly pulverized as finely as possible and dried between filter- or blotting-paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

Solution of Potassium Iodide.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

Decinormal Potassium Bichromate.—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

(*b*) *Determination*—(1) *Standardizing the Sodium Thiosulphate Solution.*—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

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(2) *Weighing the Sample.*—Weigh about 0.5 gram of fat or 0.250 gram of oil[1] on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour into the crystal and allow to cool. Introduce the watch crystal into a wide mouth 16-ounce bottle with ground-glass stopper.

(3) *Absorption of Iodine in Hanus Method.*—Add 25 cc. of the iodine solution to the fat or oil dissolved in 10 cc. of chloroform. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent. of the amount added.

(4) *Titration of the Unabsorbed Iodine.*—Add 10 cc. of the potassium iodide solution and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(5) *Standardizing the Iodine Solution by Thiosulphate Solution.*—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

[1] Use from 0.100 to 0.200 gram in case of drying oils which have a very high absorbent power.

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Per cent. of iodine absorbed:

Weight of fat taken	1.0479	grams
Quantity of iodine solution used	40.0	cc.
Thiosulphate equivalent to iodine used	62.1	cc.
Thiosulphate equivalent to remaining iodine	30.2	cc.
Thiosulphate equivalent to iodine absorbed	31.9	cc.
Per cent. of iodine absorbed (31.9 × 0.012697 × 100) divided by 1.0479	38.65	

Unsaponifiable Matter.

Wherever possible use the following method: Saponify 5 grams, or its equivalent, with 5 cc. of a 50 per cent. by volume aqueous KOH solution and 25 cc. alcohol. Heat on the water-bath for half an hour, frequently agitating at the beginning until as complete solution has been effected as is possible. Then transfer to a shallow porcelain dish, using alcohol to rinse the flask. When the alcohol is about half evaporated off, mix 10 grams of sodium bicarbonate and 25 grams of clean quartz sand, previously washed with HCl and distilled water and dried thoroughly. Add this mixture to the soap and stir together with a glass rod. Evaporate to dryness and continue the drying for several hours or over night. The mixture is then pulverized and placed in a Soxhlet extraction apparatus, where it is extracted with a low-boiling petroleum ether for four or five hours. The ether solution, containing the unsaponifiable matter is then transferred to a separatory funnel and washed with distilled water. Then filter into a tared flask, and distil off the solvent. The last traces may be removed by passing a current of air through the flask over the residue and finally drying in an oven at 98°-100° C. for four hours. The residue is weighed as unsaponifiable matter.

For oils that cannot be treated in this way on account of their forming a glutinous mass with petroleum ether, proceed as follows:

Saponify in the same manner as above and transfer to a shallow porcelain dish. Evaporate to dryness and continue to dry for several hours, or over night, but without adding sand and sodium bicarbonate. Next add about 30 cc. petroleum ether and rub it up with the soap by means of a glass rod flattened at one end. Then decant off the ether, with whatever soap may be in suspension in a finely divided condition and repeat the operation

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several times until the soap is thoroughly extracted. No less than 200 or 300 cc. in all should be used. The soap in suspension, as well as in solution is next washed out with distilled water in a separatory funnel, using a little alcohol to break up emulsions. The washing should be proceeded with cautiously at first, and the clear ether transferred to another funnel as fast as it is formed, where it may be vigorously shaken. The aqueous soap solution should also be shaken out with petroleum ether as some of the unsaponifiable matter is apt to pass into the aqueous part together with the soap. When thoroughly washed, all the ether solutions are filtered into a tared flask, the solvent distilled off, the last traces being removed by passing a current of air through the flask and drying in the oven for four hours, as above. The residue, however, may contain small amounts of fatty acids which can be determined from the acidity and a correction made.

Maumené Test.

In a tall 100 cc. beaker weigh out such a quantity of oil as when made up to 50 grams with mineral oil will not give a rise in temperature above 60° C. Make up to 50 grams with mineral oil and place in a large beaker well lined with hair. Add 10 cc. concentrated sulphuric acid of the same temperature as the oil mixture, taking one minute to add and always allowing the pipette to drain the same length of time. Stir constantly with the thermometer during the addition of acid and continue stirring until the temperature has reached the highest point. Run blank, using the same amount of mineral as for test. Deduct this rise from the total rise for the mixed oil. For specific temperature, run 50 grams of water in the same way as the sample was run. Divide the rise in temperature per gram of oil by rise in temperature per gram of water and multiply the result by 100.

Specific Gravity.

Specific gravity should be determined at 20° C., both the substance and the distilled water with which it is compared being at that temperature.

Titer Test—Provisional.

A. O. A. C. Provisional Method.

Bulletin No. 107.

(*a*) *Standard Thermometer.*—The thermometer must be grad-

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uated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be made at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about fifteen inches over all. The thermometer is annealed for seventy-five hours at 450° C. and the bulb is of Jena normal 16-inch glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched in the stem, the graduation to be clear cut and distinct but quite fine.

(*b*) *Determination.*—Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free the fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam-bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 × 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 × 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury.

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The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Melting-Point.

Take a tube of thin glass 2½ inches in length, and of such size that when the thermometer is inserted there will be about 1 mm. space between it and the glass. Fuse one end of the tube in the flame until the edges are drawn in slightly, forming a smooth, round hole. About half an inch from the other end make a small hole, either by fusing and blowing, or by filing. The tube is then ready for use. Draw a rubber band tightly over the end that was partially closed by fusion and bind on with a rubber ring. Pour such a quantity of the melted fat into the tube that when the thermometer is inserted the bulb will be a little more than covered by fat. The column of fat should then be about one and one-fourth inch in height. The thermometer, which is inserted to near the bottom of the tube is firmly secured with a perforated cork. The fat is now cooled well down below its melting-point by immersing in cold water. When this is done, take the apparatus from the cold water, remove the rubber band, and wipe dry. Then suspend the thermometer with the tube and fat attached, in an Erlenmeyer flask, or other convenient air-bath, securing it by means of a cork. Place on a water-bath and as the temperature slowly rises note the point at which the fat begins to protrude quite perceptibly, also the point at which the first drop falls and the point at which the fat becomes clear. For the latter, a small cork is inserted to prevent the fat from running out. Then remove the cork, and as the fat runs out notice its consistency, whether thin or viscous.

Cold Test—Millwood.

Warm the oil until the stearine is dissolved and filter through several thicknesses of filter-paper, into a *dry* 4-ounce wide-

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mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the thermometer, and at every degree rise in the temperature the bottle is inverted; continue until the oil runs to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

Cloud Test—Manns.

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding-point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding-point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice and water. The test is conducted as follows; the oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the dry body of the oil, the temperature at which this cloud occurs is noted.

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With care, results concordant to within 1 degree Fahrenheit can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit. The oil must be tested within a short time after heating to 150° C., and a retest must always be preceded by reheating to that temperature. The cloud-point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

COLLOID CHEMISTRY AND TANNING.[1]

By H. R. Procter.

The manufacture of leather may be considered as a problem almost purely of colloid chemistry, since the hide-fibers are merely an organized colloid jelly, and not only the tannins themselves, but the basic mineral salts used in tanning possess marked colloid character. It must be admitted, however, that up to the present, the many attempts to explain the conversion of hide into leather have been by no means wholly satisfying; and I do not propose in these pages to add another to these incomplete theories, but rather to summarize what has already been accomplished, and to distinguish between ascertained facts and assumptions which may take their place in the future explanation, but which are as yet unproved.

The hide-fiber is, as has been stated, a colloid jelly capable of swelling largely in water, and chemically most closely allied to ordinary gelatine, into which it rapidly changes on heating with water. The other constituents of the hide, such as yellow elastic fiber, and albumins, if they cannot be altogether disregarded in a theory of the tanning process, at least play a very subordinate part in it. Practically the greatest complication in this respect arises from the organized structure of the fibers, which are bundles of extremely tenuous fibrils of about 0.001 mm. diameter. The material by which these fibrils in the unaltered hide are cemented into bundles has been the subject of much discussion[2] and it is yet uncertain whether it differs from the

[1] Reprinted from the "*Gedenkboek—van Bemmelen*," 1910.

[2] Rollet, *Sitz. ber. Wien. Akad.*, 39, 305; Reimer, *Dingl. polyt. Journ.*, 205, 153 *et seq.*; Van Lier, *Hoppe-Seyler's Zeitschr. für physiol. Ch.*, 61, Heft 2.

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fibrils themselves in any other way than by a greater degree of hydration; but for the purposes of the present enquiry its nature is of secondary importance, since in practice it is largely if not wholly removed previous to tannage by the solvent action of alkaline or acid liquors. It may be mentioned, however, that even in the dissolved condition, it enters into insoluble combination with the tannins, and with most other tanning substances; in this respect resembling the earlier hydrolysis-products of gelatine.

When placed in cold water, the hide-fiber swells; but like gelatine, not indefinitely, but to a fixed maximum. During the earlier stages of the swelling considerable mechanical pressure is exerted; and judging by analogy, heat is evolved; though the author is not aware that it has been experimentally determined. As the swelling approaches its maximum, the mechanical energy becomes very small, and the heat evolved is insensible. It is clear that we have here a case of osmotic pressure of an ordinary character, in which the attraction of the fiber-matter for water is balanced against that of its own cohesion; and both forces must diminish as swelling proceeds. In order that there may be a maximum, the attraction for water must diminish more rapidly than the cohesion. At higher temperature this ceases to be the case, and the swelling proceeds to complete colloid solution. The position of the maximum is not a fixed one, but may be varied by the previous history. It has been shown by the author that that of gelatine is partially dependent on its original setting volume, and both in this case, and that of hide it is influenced by the temperature and possibly by other conditions of the previous dehydration, since both hide and gelatine after drying at high temperature show very little tendency to swell, and even in hot water are dissolved with great difficulty.

Both in acid and alkaline solutions the swelling is greatly increased, and the maximum is much raised. In acid swelling, which has been specially investigated by the author, gelatine which will absorb 7 or 8 times its weight of pure water may swell to over 50 times in very dilute acid; and in the stronger acids, and typically in hydrochloric acid, a maximum swelling is obtained at a dilution of below 0.01 millimolecular concentration; and gradually diminishes with increasing concentration till actual

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solution begins; and hide-fiber behaves in quite an analogous way, though the maximum is lower owing to its greater cohesion. It is clear that in both these cases two separate kinds of absorption are concerned; firstly the direct attraction of fiber for acid, and secondly the mechanical absorption of acid liquid by osmosis. It is not possible at present accurately to determine what proportions of the actual acid absorbed are due to each of these forces, but that they are of different character is proved by the fact that while the whole of the absorbed acid can be estimated by titration with caustic alkali using phenolphthalein as an indicator, a considerable part is no longer capable of reddening methyl-orange, indicating that it does not ionize to a greater extent than about 10^{-6} millimolecular hydrion concentration. The actual quantity of hydrochloric acid fixed in this way increases with increase of concentration, at first rapidly, and afterwards more slowly, tending to a maximum of about 1.25 mols. per 1,000 of dry gelatine. The osmotic swelling of acid gelatine can be almost wholly inhibited by the concentrated solution of an alkaline chloride (though on neutral gelatine such solutions slightly increase swelling); and under these conditions the total maximum absorption is somewhat greater than that not indicated by methyl orange. The behavior of sulphuric acid with concentrated sodium sulphate solution is almost identical, taking into account its dibasic character.

If the provisional assumption be made that the acid solution absorbed osmotically is of the same concentration as that of the exterior solution, an almost constant excess is absorbed, amounting with most acids to about 0.8 mols. per 1,000 of dry gelatine. It is, however, quite clear that the underlying assumption is only approximate, as the very fact that chloride solutions exert an external osmotic pressure on the gelatine when acidified with hydrochloric acid proves that the acid gelatine must inversely expel chlorides, (including hydrogen-chloride) from the absorbed solution, and consequently, the latter must be weaker, and the amount of fixed acid larger than that shown by the calculation; and it is quite probable that if an adequate correction could be applied, the results would agree closely with those of the two methods already mentioned. The quantitative results are in

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agreement with the ordinary equations for the hydrolyzable salt of an acid with a weak base.

The results of alkaline swelling so far as they have been investigated are very similar in character, suggesting a definite hydrolyzable compound of a weak (amphoteric) acid with a strong base, and the evidence in both these cases points strongly to ionic chemical combination, though it cannot be said to be yet actually conclusive.

The swelling in the case of acids is obviously dependent in general terms on hydrion concentration, and in the case of alkalies, on that of hydroxyl-ions, but in both cases perplexing anomalies occur, and it is pretty clear that with acids the anions, and with alkalies the kations also have their share in the reaction. Thus the swelling by hydrochloric acid is repressed by alkaline chlorides, while that caused by sodium hydrate is unaffected by neutral sodium salts but repressed by excess of hydroxides; but on the other hand it has been shown by Stiasny[1] that the swelling produced by different hydrates varies in character and firmness, and that these differences continue even when the different hydroxyl concentrations due to differences of ionizability are compensated by varying the strength of the solutions.

Investigations of the absorption of vegetable tannins, as well as of the metallic basic salts capable of producing leather, while somewhat inconclusive, point rather to adsorption than to chemical combination as the leading factor, at least in the first stages of the process.

It should not be forgotten, however, that the tanning action of salts such as those of chromium and aluminium is a complex one, in which both effects are probably involved, the acid combining chemically, and the colloid salt physically with the hide-fiber. Thus in the case of ordinary tawing with alum and salt, the hydrolyzed acid of the mixture is rapidly absorbed by the fiber, leading to further hydrolysis and production of a basic and more or less colloidal aluminium salt which is itself absorbed, while the common salt present in the mixture dehydrates the fiber osmotically, preventing swelling, and enabling the fiber to carry a larger quantity of acid. It is clear that if this be ad-

[1] *Gerber*, 32, 200 *et seq.* (1906).

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mitted, investigations as to the salt primarily absorbed, such as those of Reimer[1] and Krutvig[2] are useless, since, though on the whole the acid and base is absorbed in the proportions present in the mixture, their exact relation is dependent largely on physical conditions. In the case of aluminium tannage the action is usually allowed to stop at the point of equilibrium with the solution, and the resultant leather is in part a true aluminium tannage, and in part a mere physical product of the action of the acid and salt, which by dehydrating the individual fibrils prevents their adhesion on drying. This view is strongly supported by the effect of water on this kind of leather, which by removing the common salt, permits the swelling action of the acid, and at the same time dissolves a considerable part of the absorbed aluminium salt, leaving, however, a permanently hydrolyzed and basic portion so that while the washed leather dries hard and horny, it does not completely return to the condition of untanned pelt. In basic chrome tannage, the process is usually carried a stage further. The primary absorption of chrome is favored by the use of a solution already made basic, so that the fixation of a given quantity of acid corresponds to that of a larger proportion of base, and the resultant leather next undergoes so-called "neutralization," which consists in the removal of the excess of absorbed acid by a weak alkaline bath, and the consequent permanent fixation of the chrome in a basic and colloid form. In most other tanning processes a more or less complete fixation is obtained either intentionally, or as a result of natural changes in the absorbed matter, the nature of which is often difficult to explain. Even in alum tannage considerable fixation takes place on "aging" or keeping for some weeks, after which a much smaller proportion of the alumina salt can be washed out. It is possible that, in some cases of organic tannage, oxidation takes part in this fixation, as has been supposed by Dr. Fahrion,[3] but it seems to the writer too much to assume that this is universally the case. Owing to the fixation just spoken of, the tanning process is usually irreversible, and no definite absorptive equilibrium can occur, since

[1] *Dingl. polyt. Journ.*, 205, 153 *et seq.*

[2] *Rev. univ. des Mines*, 1899; *Collegium*, 1902, 161.

[3] *Zeits. f. angew. Ch.*, 22 (1909); Comp. Meunier and Seyewitz, *Collegium*, 1908, p. 195 *et seq.*

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the insoluble portion no longer takes part in it; and this irreversibility is of course essential in most cases to the production of commercially valuable products, since otherwise on exposure to water, the tanning matter would dissolve out, and the fiber return to the condition of raw pelt. In many cases, however, the fixation is very incomplete and much of the tannage may be washed out, as for instance with alum and with some vegetable tannins. It may be supposed, therefore, that the original absorption of the tanning matter is usually a physical adsorption either by the mechanical surfaces of the fibers, or of a more intimate nature within the substance of the jelly;[1] while the fixation may in some cases be due to chemical action, but is often analogous to the change from sol to gel, or to the mutual precipitation of two oppositely charged colloids. It appears that a neutral gelatine free from electrolytes possesses no electric charge[2] and does not precipitate a pure tannin solution, but in acid solution takes a positive charge as compared to the liquid, and in an electric current wanders to the kathode, while tannin particles are negative. All practical tanning operations must be carried on under acid conditions, the only marked exception being that of formaldehyde, which acts best in alkaline solution, but obviously presents little analogy either to the organic tannins, or to the more or less acid solutions of basic salts. Apart from its effect in cataphoresis, the exact function of the acid in vegetable tanning is not easy to explain. Mr. Arnold Seymour-Jones, working in conjunction with the author, has investigated the subject but the results are somewhat ambiguous, and vary with different tanning materials and acids. It is obvious that the function is a complex one, related not only to the electric charge, but to the swelling of the fiber; and the time occupied in diffusion through it; and it is purposed to carry on the investigation, in the hope of clearing up these points. In this connection, what has been said of the osmotic effect of salt solutions on acid gelatine and hide-fiber should not be overlooked. By the mere action of acid and salt, the pelt can be so altered as to possess all the physical properties of white leather so long as it is kept dry; and Knapp[3] has shown that a similar

[1] Comp. Herzog and Adler, *Collegium*, 1908, p. 178.
[2] Hardy, *Journ. of Physiol.*, 24, 288-304 (1899).
[3] "Natur und Wesen der Gerberei," Braunschweig, 1858.

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effect may be produced by mere dehydration with alcohol.

Knapp's theory developed in the brochure just cited that all tanning was due merely to surface-coating of the hide-fibers which prevented their adhesion, has proved insufficient to explain all the known facts, and there is little doubt that not only actual chemical changes occur, but also physical absorption which is rather molecular than merely mechanical, but there can be no question that in certain cases actual coating of the fibers does take place. Knapp showed that by treating alcohol leather with an alcoholic solution of stearic acid its softness and permanency was much increased, and in many fat-tanning processes, mechanical coating though not the sole action concerned, yet plays its part. It must also be mentioned that in the later stages of sole-leather tanning, when the fiber has fully absorbed its fill of soluble tannin, the deposition of ellagic acid and other difficultly soluble products of the tanning materials on and between the fibers still continues and contributes much to the solidity of the finished product.

Finally, it must be repeated that no single explanation will cover all the very various ways of making leather, and that while Knapp's original dictum that the essential condition is the isolation and non-adhesion of the fibers remains true, there are many ways in which this can be brought about.

Leeds, Aug., 1910.

THE VALUATION OF MINERAL LEATHER OILS—LABORATORY TESTS.

By Charles R. Oberfell.

The value of mineral oils in the leather industry has been proved, and they are coming into more extended use every year. Some, of course, are of very fine quality while many are unsatisfactory. It devolves upon the chemist for the leather manufacturer to determine the suitability of these oils, and it has been his task up to the present to select whatever tests he deemed would give him the value of the oil, and to use any of a number of methods to obtain results on these selected tests.

Many of the characteristics obtained on an oil used for lubrication can be interpreted in the valuation of a leather oil. For example the viscosity, gravity, cold test, evaporation, etc., are

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determined on leather oils and are of value when the chemist has collected sufficient data to make proper comparisons.

This Association might consider whether or not this is a suitable field for investigation. Methods for the analysis of mineral leather oils should be standardized, in order to forestall the possibility of confusion with which the oil chemist is dealing to-day. One illustration will show the necessity of this. If a sample of lubricating oil is sent to say six chemists for viscosity test the results will more than likely all be different, because the probability is that they will use different forms of apparatus to determine this characteristic. How simple and desirable it would be for the Association to prescribe a viscosimeter on which all mineral oils used in the leather industry would be tested and thus help to eliminate differences between buyer and seller, and make possible the accumulation of data whereby an oil could be readily valued.

Chemically, mineral leather oils do not differ from mineral lubricating oils, but in the case of the lubricating oils the exact conditions under which they find service can be ascertained, as area of surface to be lubricated, character of bearing, speed and load, while leather oils are subject to any number of unknown factors; character of leather and tannage, condition of leather when oiled, atmospheric conditions during drying, etc. On account of this difference there is a greater latitude in the interpretation of the chemist's report and necessarily some modifications in analytical procedure is made. The flash test of an oil to be used as a lubricant can be taken as indicating the class of work on which the oil can be used, while for greasing leather the same will probably be used to indicate whether or not the oil might impart a harshness to the finished product.

The following tests suggest themselves as being useful, but all are perhaps not essential.

A.—Specific gravity.
B.—Viscosity.
C.—Evaporation.
D.—Flash point.
E.—Burning point.
F.—Acidity.
G.—Alkalinity.
H.—Color.
I.—Cold test.
J.—Cloud test.
K.—Purity.
L.—Asphaltic bases and tar.
M.—Saponification matter.
N.—Sulphur.
O.—Penetration.
P.—Emulsification.

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A. *Specific gravity.*—The gravity is essential as from it the weight per gallon of an oil is obtained. It may also be useful in forming an idea as to the source of the oil; whether Texas, Pennsylvania or Mid-Continent crudes were used. The methods for determining the gravity are too well known to discuss, but there are certain forms of apparatus in use which have inherent faults and these must be guarded against.

B. *Viscosity.*—This test is of importance as it gives the body of the oil, which when considered with the weight leads to an idea of how the oil will remain on the leather. An oil which is heavy and of low viscosity will obviously "drip" more than an oil in which these characteristics are not so far apart. The viscosity also tends to determine the penetrating ability and will be considered under penetration test. For viscosity determination there are many forms of apparatus. The essential points to be considered in its selection are uniformity and cost. The viscosity should be taken at a normal temperature; one at which the oil is generally used.

C. *Evaporation.*—This test will indicate the completeness of refining or the amount of matter present which is volatile at low temperatures. The effect of these "light ends" must be determined, but present knowledge points to their imparting a harshness to the finished grain. As to its determination it is essential that a uniform procedure be in use, for widely varying results can be obtained by different methods. It is necessary to specify the amount of oil to use, temperature, time of heating and form and size of dish in which the oil is exposed.

D. *Flash point.*—In a manner this supplies the same information obtained by the evaporation test, for an oil of high percentage of volatile matter will have a low flash point. The relative value of these tests must be determined, and here also a choice of apparatus is possible. Whether an open or closed cup with mechanically timed test flame is used it is to be decided, but it should be the same in all cases. Here too, the cost of the apparatus is a factor after uniformity is secured. The open cup is in general use.

E. *Burning point.*—At present this test finds no useful application unless it may enable the analyst to form an idea of the source of the crude petroleum.

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F and G. *Acidity and Alkalinity.*—The presence of either indicates an imperfectly refined product. Their effect is well known and a high class oil should be free from both. Their detection is largely qualitative which presents no difficulty.

H. *Color.*—Whether a perfectly refined, well balanced oil of dark color will impart a less desirable color to leather than one of lighter shade is a matter of speculation. The writer believes that other things being equal, unless the oil is very dark or black, the color has little influence.

I. *Cold test.*—The values for this may vary over a comparatively wide range and make little difference. Unless the oil congeals at a very high temperature the leather manufacturer is not interested. If the test were of greater importance it should receive careful attention at the hands of the leather chemist. Great variation exists in the methods in use. The amount of oil, rate of chilling, time the oil remains in the chilling mixture, etc., are all points in which uniformity is needed.

J. *Cloud test.*—The amount of paraffines present or the behavior of the oil during chilling may be of importance in applying oil to leather during cold weather. The remarks under cold test equally apply here.

K. *Purity.*—An oil which contains water or is turbid can not have the same value as a clear, moisture free oil. The methods for use here are optical.

L. *Tar and asphaltic bases.*—Their presence in any amount may lead to poor color or smeared appearance. A clear solution with 84-88° gasoline readily settles the matter.

M. *Saponifiable matter.*—Whether or not a mineral oil is adulterated with inferior animal or vegetable oils is a matter of importance. Their detection and estimation is well known.

N. *Sulphur.*—If sulphur is of importance it can only be in determining whether or not an oil refined from a crude containing sulphur is suitable for leather dressing. Sulphur in itself should have no reaction and the oxidation of the sulphur is not probable. This point is open to discussion and the writer considers it well worth determining. The sulphur-lamp method where the products of combustion are taken up in sodium carbonate solution is in common use among oil chemists, but is very

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tedious and has constant sources of error. A proposed method follows.

O. *Penetration.*—The less body an oil has the easier it will penetrate, but this is not an arbitrary property as the weight of the oil determines how thin it may be. No methods are known for this property, but it is hoped that the leather chemists can develop a substantial one as it will greatly aid in valuating an oil for leather dressing.

P. *Emulsification.*—A mineral oil which forms a creamy emulsion will penetrate the leather fibers well, and in addition on its ability to hold the emulsion depends its remaining in the leather during drying. If a test can be developed which will give the emulsifying property of an oil, a solution of the penetration test will be at hand.

The following methods, collected from various sources, are in use in the writer's laboratory and are submitted not in the thought that they are the best, but because they have served a useful purpose and may form a nucleus from which other and better methods may be developed.

SPECIFIC GRAVITY.

The Westphal balance, on account of its convenience, is used when there is sufficient sample. The oil is cooled to 15.5° and placed in a water-bath, at this temperature, during balancing. When sample is small a pyknometer having a capacity of 25 grams is used. The pyknometer is filled at about 14.0° the stopper inserted and then placed in a bath which is kept at 15.5° until no more oil rises from the capillary tube. The weight of the oil is obtained by multiplying the gravity by the weight of a gallon of distilled water at 15.5°.

EVAPORATING TEST.

Weigh approximately 0.2 gram of oil into a flat bottom heavy glass dish; 8 mm. deep and 50 mm. diameter. Place in an air oven, the temperature of which is nearly constant at 60-65°, and heat for 8 hours. It is then cooled and weighed. The loss is calculated in percentage.

FLASH POINT.

Set a porcelain crucible, 60 mm. top diameter, 25 mm. bottom diameter and 50 mm. in height in a sand-bath so that the top of

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the crucible is below the rim of the sand-bath. Fill the crucible with oil to within ¼ inch of the top, adjust the thermometer in the center of the liquid. Apply heat so that the temperature of the oil rises 8° per minute and apply test flame first at 150° and then at every rise of 2.5°. A jet flame can be obtained by using a glass tube drawn out until it gives a flame 8 mm. long and 3 mm. diameter. Apply the flame by passing it slowly and completely across the crucible about ½ inch above the level of the oil and just in front of the thermometer. The flash point is the lowest temperature at which the vapors of the oil flash and go out.

BURNING POINT.

Continue the heating after the flash point is determined. Applying test flame as before until the vapors catch fire and burn over the surface of the oil.

VISCOSITY.

For a cheap and thoroughly reliable instrument for leather work the Dudley pipette used by the chemists for the Pennsylvania R. R. is used. This pipette is graduated to hold 100 cc. at 70° F. and will deliver 100 cc. of water at 70° F. in 34 seconds. The pipette should be enclosed in a box with a sliding glass front and metal bottom for heating the oil contained in a metal beaker. A thermometer passes through the top of the box into the beaker and another one extends into the box so that the oil and the temperature of the interior of the box will be the same. Bring the oil to 20°. See that temperature of the box is the same. Allow the oil to flow and record number of seconds required. Report in number of seconds or in degrees obtained by dividing the number of seconds by 34.

REACTION OF OIL.

Heat about 15 grams of the oil with 50 cc. distilled water, draw off the water and test its reaction with litmus. If the reaction is acid it is probably due to sulphuric acid which is tested for with barium chloride.

ASPHALTIC BASES AND TAR.

Place 5 cc. of the oil in a pear shaped separatory funnel of about 200 cc. capacity, add 95 cc. 84-88° gasoline, shake well and allow to stand 15 minutes. No precipitate should appear.

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COLD TEST.

Place 50 cc. of the oil in a 4 ounce vial bottle, provided with a stopper through which passes a short stout thermometer. Place in a chilling mixture and stir occasionally until the oil has solidified. Insert the stopper and allow the bottle to remain in the chilling mixture one hour. Remove, wipe dry and place in a beaker containing dry asbestos wool to insulate the bottle. Stir the solid oil with the thermometer, invert the bottle frequently and note temperature at which the oil flows from one end to the other in 15 seconds. For chilling mixture use ice and salt or if necessary crystallized calcium chlorid and snow or shaved ice.

CLOUD TEST.

Use bottle, amount of oil and thermometer as in cold test. The cloud test or chilling point is the temperature at which flakes or scales begin to form in the liquid. It is determined by cooling the oil 5° at a time with occasional stirring and constant watching.

SAPONIFIABLE MATTER.

(Qualitative)

Heat 5 cc. of the oil in a test-tube with a piece of sodium hydroxide for 15 minutes at 230°-250°. Cool. Saponifiable matter is indicated by the gelatinization, complete or partial of the contents of the tube.

(Quantitative)

For all practical purposes determine unsaponifiable matter (Mineral Oil) by the A. L. C. A. Provisional Methods for the analysis of oils and fats. The difference between this and the amount of original oil taken represents the portion saponified.

SULPHUR.

(Tentative method)

To 25 grams of the oil in a porcelain dish add 2 grams of dry sodium carbonate and evaporate cautiously to a thick syrup. Ignite with the gradual addition of small amounts of ammonium nitrate until the ash is white. The residue is taken up with dilute HCl, filtered and the sulphuric acid estimated in the filtrate as barium sulphate. A preliminary test for free sulphuric acid is required.

Harrisonburg, Va., Nov., 1910.

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ABSTRACTS.

Chestnut Extract. U. J. THUAU. *Le Cuir*, Nov. 15, concluded from Nov. 1.—Two methods of extracting are used. In the first the vats are open; in the second, closed vats called autoclaves are used, and the extraction takes place under a pressure of two atmospheres or more, at temperatures ranging up to 130° C., (266° F.). Experiment has shown that the yield of extract increases with pressure up to two atmospheres, (121° C., 250° F), but decreases at higher pressures and temperatures. Excepting mimosa bark, valonia and sumac, whose tannin decomposes at temperatures above 60° C., (150° F.), almost all tanning materials may be extracted at the boiling temperature without sensible decomposition of the tannin. Above this temperature a part of the tannin decomposes into pyrogallic, gallic and ellagic acids, into pyrocatechin, into anhydrides of tannin, or into glucose.

When the extraction is done under pressure, there is a larger yield of tannin and a little more non-tannin, but a part of the tannin which has been extracted is converted by the heat into non-tans, and this results in an extract differing materially in composition from that made in open vats. An average analysis of chestnut extract of 25° Baumé made in open vats is as follows: Tannin, 32 per cent., non-tannin, 7.3 per cent., insolubles, 0, water, 60.7 per cent., while an extract made under a pressure of two atmospheres gave an average of: Tannin, 29.8 per cent., non-tan, 12 per cent., insolubles, 0, water, 58.2 per cent.

Some extract factories use green chestnut wood, but because of the high moisture content of the wood, they obtain a poor yield. Most manufacturers, however, pile the wood to dry before using it. The extracting vats are grouped in series of 5, 7, 9 or even 12, containing from 6,000 to 12,000 liters (1,500 to 3,000 gallons) each. The open vats are made of wood or copper, the autoclaves of copper or bronze. An autoclave of 12,000 liters holds from 4,500 to 6,000 kilos (5 to 6⅔ tons) of wood. The liquor passes in succession through all the vats, over wood less and less spent, and finally over new wood, the fresh water passing into a vat in which the wood is nearly spent. The temperature is highest in the first vat, containing nearly spent wood, and diminishes gradually. The strength of the liquors thus obtained is from 3 to 4½ degrees Baumé, (22° to 33° barkometer).

They are clarified and decolorized by special methods, blood being much used.

The liquors are then concentrated in vacuum evaporators, multiple effect apparatus being employed, sometimes with as many as six effects. The yield of 25° Baumé extract from different chestnut woods varies from 15½ per cent. to 23 per cent. for wood which has been in storage a year.

Chestnut extract is used chiefly by sole leather tanners. It costs from 75 to 85 centimes per kilo of tannin, (7 to 7¼ cents a pound). It is not, properly speaking, cold soluble, but dissolves readily at 60° C.

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Chestnut extracts treated with sulphite or Solvay soda are not very desirable, as they oxidize in the air and give a dark color. The best extracts are those which, rich in tannin, remain clear under the oxidizing action of the air.

It is to the interest of the makers to use the pressure-extraction method because of the greater yield. :Some makers, however, continue to use open vats, encouraged by the higher price of the product.

A chestnut extract rich in non-tans penetrates slowly, while the penetration is more rapid if the non-tan content is less. The conditions in the case of vat tannage are different from those of drum tannage. In the former case the proportions of tannins and non-tans absorbed by a hide from chestnut extract are about 20:1, while a drummed hide will absorb one-fourth as much non-tan as tan. This latter proportion is near the average of that found in chestnut extract, so that in drum tannage the hide absorbs the extract whole, so to speak. Since non-tans in leather are easily extracted by water, a high percentage of them tends to lower the quality of the leather. It may be stated, therefore, that for drum tannage the better extract is that which for a given tannin content has the lower proportion of non-tans.

For vat tannage, however, the conditions are different. An extract rich in non-tans, while it penetrates more slowly, plumps better because of its larger proportion of glucose and organic acids, and a part of the anhydrides of tannin may be hydrolyzed and transformed into tannin, thus giving a high yield. Extract poor in non-tans has the advantage of penetrating more quickly, but it gives a lower yield, and because it furnishes less non-tans to the leather, the leather ought to be better.

Acid in Chrome Leather; Determination of Free ——. G. GRASSER. *Collegium*, 1910, pp. 381-382.—The qualitative test for free acid in chrome leather by pressing test-paper against its cut surface is not always conclusive owing to the strong affinity which the acid has for the leather fiber. The following method for determining free acid in chrome leather is stated to be reliable and quick and also shows any excess of alkali in de-acidified leather. 20-30 grams of the finely divided leather are made into a thick paste with distilled water in an Erlenmeyer flask. 30-40 cc. of N/1 hydrochloric or sulphuric acid are added, the flask connected with a reflux condenser, and warmed with the naked flame until the leather particles are completely dissolved (½-1 hour). The interior of the condenser is then washed into the flask, which is cooled and the contents titrated with N/1 alkali using methyl orange as an indicator. Any access of alkali required over that necessary for neutralization of the N/1 acid used represents the free acid derived from the leather and in a similar way any access of alkali in the leather is shown. If the presence of green chromium salts renders the determination of the end-point difficult, litmus is used as an external indicator. Through the decomposition of the leather all chromium is brought into solution and chromic acid and chromates are reduced to chromium salts. The chromium origi-

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nally present in the leather can therefore be determined in the solution, but a volumetric process must be used, since the presence of organic matter hinders the precipitation of chromium as hydroxide.—Abstract from *J. S. C. I.*

Employment of Cold in the Leather Industry. W. EITNER. *Der Gerber,* Oct. 15 and Nov. 1, 1910, pp. 279-293.—The rapid cooling of hides immediately after removal as carried out in the packing houses of America and Argentina, is an advantage because it tends to prevent the incipient decay due to the blood, etc., in the hide, which would otherwise take place before the salt could arrest the action of bacteria present in and on the hide. The temperature for this purpose should be below 10° C. (50° F.) but the hides must not be frozen, as the expansion of the water in freezing tears apart the hide-fibers and weakens the leather made from such hides.

Wet salted hides keep more perfectly in cool storage-houses than in warm ones. The stone vaults formerly used for hide storage were admirably adopted to keep the hides at a nearly uniform temperature.

Dry salted hides after the sweating process were formerly hung in cold running water for some weeks, to sterilize them. This is now done in a few hours by chlorine, sulphurous acid or formaldehyde.

In the tanning process, low temperatures are not desired, as the reaction between hide substance and tanning material, whether vegetable or mineral, does not go on below 12° or 15° C., (44° or 50°F.). Formerly, however, owing to the unclean conditions in the tanneries and the failure to destroy the germs of unfavorable fermentations before the tanning was begun, the high temperatures of summer sometimes caused the hides to decay in the tan pits, so that ice had to be used to prevent the liquors from becoming too warm.

One strange use of cold in the making of leather was the so-called "tanning of the Holy Simon." Leather tans slowly and poorly in the winter, and if it was necessary to hasten the finishing of stock to fill orders the half-tanned hides were laid out to freeze. After this the tanning materials penetrated quickly, but the quality of the leather was much lowered.

An important use of cold is in the clarification of extracts, a process which is being patented by the firm of Dr. A. Redlich. Quebracho extract, made under pressure, is immediately cooled rapidly to below 10°. The heavy resinous dyes soluble above 100° are thus separated in the form of large flakes, and they carry down with them the materials which would othewise deposit slowly and be difficult to remove. By this method a bright, clear, rapidly penetrating extract is produced.

Scientific Investigation as Applied to Tanning. L. JABLONSKI of Berlin. In *Shoe and Leather Reporter* of Sept. 22, 1910, p. 41.—The writer calls attention to the importance of analyzing the waters used in the beam-house, in order to determine what substances should be put into the soaks, and of careful experiment to determine what treatment here

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gives the best results. He recommends the analysis of the lime used, in order to avoid introducing into the limes argillaceous earths, which partially tan the hides, and spoil the quality of the leather. The time requires for liming should be determined as closely as possible, in order to avoid loss of hide substance by liming too long.

He recommends testing with phenolphthalein to determine when deliming is finished, and calls attention to Professor Procter's suggestion to use sal ammoniac or sulphate of ammonia in the last stages of deliming in order to avoid danger from free acid.

Constituents of Candelilla Wax. G. S. FRAPS AND J. B. RATHER. *Journal of Industrial and Engineering Chemistry,* November, 1910, p. 454. —This hard opaque, nearly white wax is from the candelilla or Mexican wax plant. Suggested uses for it are:—Candles, shoe polish, phonographic records, electric insulation, beeswax substitute.

Its constants as determined by Deiler, and by Hare and Bjirregaard, and the corresponding constants of beeswax are given in the table.

	—Candelilla wax—		
	Deiler	Hare	Beeswax
Specific gravity at 100° C.	0.87	.....	.....
Specific gravity at 15° C.	....	0.98	.....
Iodine number	14.0	36.8	6—13
Acid number	19.0	12.4	19—21
Ester number	40.7	....	73—76
Saponification number	59.7	64.9	.....
Melting point	66° C.	67°-68° C.	.....
Unsaponifiable matter, per cent	.....	91.17	.....

The wax is completely soluble in chloroform and carbon disulphide.

By extraction with ether for 40 hours, 40 per cent. of the wax was extracted and the dissolved matter was purified and crystallized. It seems to be the hydrocarbon hentriacontane. The crystals are small and white; melt at 68° C.; soluble easily in carbon tetrachloride and in chloroform, but not in cold alcohol.

Further extraction with boiling ether gave another white crystalline substance, probably also a hydrocarbon, melting at 85° C.

Rapid Saponification of Fats for Titer Determination. CHAS. V. ZOUL. *Journal of Ind.* and *Eng.. Chem.,* Nov., 1910, p. 479.—The method substitutes glycerine for water or alcohol as a solvent for the potash. 95 per cent. glycerine was found unsatisfactory, especially with neutral fats, it being necessary to boil off the 5 per cent. of water before saponification began.

120 grams of H. G. glycerine are placed in a 6½ in. porcelain casserole, 25 grams of KOH added and heated over a flame. The potash dissolves easily. The fat (100 grams) is now added and stirred with continued heating. The fat dissolves in 1 minute, with slight foaming in the case of refined fats. Heating is continued until the liquid becomes quiet and homogeneous, indicating complete saponification. The melt is now taken off the flame and from 15 to 30 cc. of water added from a

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wash-bottle, a little at a time, waiting each time for the foaming to subside. Dilute acid is then added to break up the fatty acids, which precipitate in a milky form and separate into a layer on slight heating. The acid must be added in small quantities, with repeated stirring. Hot water is added, and the whole placed on a steam-bath for washing. The whole time consumed may be as little as 10 minutes. The method is less satisfactory with low grade fats.

Improvement on the Wiley Method for Determining the Melting-Point of Fats. HARRY STEENBOCK. *Jour. Ind. and Eng. Chem.*, Nov., 1910, p. 480.—A serious difficulty with the Wiley method is due to occluded bubbles of air in the fat discs, which expands and carry the discs to the surface.

The author dropped melted fat on cold mercury. The discs were removed when thoroughly hardened, by means of a cold steel spatula, and thrown into cold 50 per cent. alcohol. The vessel of alcohol is then set in a vacuum desiccator and exhausted until bubbles cease to be given off.

Scott Oil Tester. *Jour. Ind. and Eng. Chem.*, Nov., 1910, p. 482.—This instrument is made by E. H. Sargent & Co. under the direction of Mr. D. G. Scott of Chicago. It substitutes an electric spark for the usual flame jet in testing for flash-point. It may be used over a wide range of temperatures. The instrument is self-contained occupying only 8 x 10 inches of space, and is 16 inches high. The sample required is very small and danger from fire is precluded.

A New Indicator for Alkalimetry and Acidimetry. PROF. DR. R. MELLET. Lausanne; *Chemiker Zeitung*, No. 121, 1073.—The author has investigated the 4-amino-*m*-oxybenzoic acid and its derivatives, of which only the methylester (orthoform) and the ethylester had up to this time been produced, in the endeavor to prepare the corresponding diazo-derivative, and to unite it with phenol and naphthol products, in order to obtain red or violet azo-dye. Among the azo-dyes analyzed, the combination of 4-diazo-*m*-oxybenzoic acid with β-naphthol, proved very sensitive to acids and bases, as it yielded highly characteristic red and violet coloring. The alkali salts of this dye are very soluble in water (violet color), while the acid itself (red) is insoluble in it.

If a mineral acid is added to the alkaline solutions, as for example dilute hydrochloric acid, the color changes to a bright red, remains for a few minutes in a colloidal form and then precipitates. It is not therefore recommended to use the β-naphtholazo-*m*-oxybenzoic acid as an indicator, at least not for titrations which require a certain amount of time. In order to obtain a soluble product the β-naphthol was replaced by one of its sulpho derivatives, forming sulpho-β-naphtholazo-*m* oxybenzoic acid which is easily soluble in water (with a red color) and whose alkali salts give a violet solution. The diazotizing of the 4-amino-*m*-oxybenzoic acid results in a yellow powder of great instability which is an anhydride.

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The union of this diazo-acid with 6-sulpho-β--naphthol results easily in an alkaline solution; the tri-sodium salt is immediately formed. In this form the new substance is most easily produced pure. The acid itself can be easily freed from its sodium salt by hydrochloric acid.

Properties and use as an indicator in Alkalimetry and Acidimetry.—The 6-sulpho-β-naphtholazo-*m*-oxysodiumbenzoate produces a deep violet powder which is very easily soluble in water, and gives an intense violet solution. With excess of alkali this solution becomes cherry red with acids, it changes quickly to red, without forming a precipitate. The 6-sulpho-β-naphtholazo-*m*-oxybenzoic acid is likewise very soluble in water with an intense brilliant red color (in very dilute solutions the color is orange red). Alkalies change this red liquid immediately to dark violet as soon as the neutralization point is reached. This indicator cannot be used like litmus in the form of test-paper, because the red paper on contact with concentrated alkali changes directly from deep red to cherry red; therefore shows no sufficiently clear color change. As test-paper it is therefore only sensitive to acids or to very dilute alkalis. On the other hand it is very good to use for titrations of alkaline and acid solutions, and because of its great dyeing ability and its sensitiveness it appears to be superior to most indicators now in use except phenolphthalein. Its solution does not become moldy like litmus solution, but remains unchanged. It is sensitive to all mineral acids, most organic acids and all bases, including ammonia. A few preliminary results are given which have to do with the sensitiveness of this new indicator as compared with those commonly used. The indicator used for these titrations was a 1 per cent. solution of the sodium salt, to which N/10 HCl was added drop by drop until it showed a clear red color.

In comparison with a litmus solution of the same weight this possesses thirty times as much color.

Determination of sensitiveness and comparison with a few common indicators.—It is well known that the color change of an indicator does not depend only upon the absolute quantity of acid or base to be titrated but also upon the amount of dilution. Methylorange, entirely loses its usefulness with solutions more dilute than N/10. This loss of sensitiveness is due principally to the hydrolization and electrolytic dissociation of the indicator, which can be recognized by the intermediate colorings appearing in the course of the change. Investigation of the sensitiveness of indicators with different concentrations, which were carried on by Robert Thomson[1] in 1883 and then by Glasser[2] in 1901, gave the following results. 1. That the various indicators could not be used without distinction when solutions are to be titrated whose concentration deviates noticeably from that of the normal solution. 2. That the same indicator when used for the neutralization of a like quantity of acid requires an entirely different quantity of base according to the dilution

[1] *Chem. News*, 1883, **47**, p. 123.

[2] Glaser, *Indicatoren der Acidimetrie und Alkimetrie*, Wiesbaden, 1901.

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of the base, and *vice versa*. 3. That neutralization cannot be reached in both directions with an equal quantity of normal solution.

1. Titration of N/100 HCl with N/100 NaOH.

	For 10 cc. HCl			For 20 cc. HCl			For 40 cc. HCl		
	a	*b*	*b—a*	*a*	*b*	*b—a*	*a*	*b*	*b—a*
Phenolphthalein...	10.0	..	..	20.0	..	..	40.0	..	..
Litmus.....	9.5	9.9	0.4	19.6	20.05	0.45	39.8	40.5	0.7
Methylorange.....	9.0	9.7	0.7	18.3	19.5	1.2	36.2	38.7	2.5
New indicator.....	9.8	10.0	0.2	19.7	20.05	0.35	39.8	40.1	0.3

2. Titration of N/100 NaOH with N/100 HCl.

	For 10 cc. NaOH			For 20 cc. NaOH			For 40 cc. NaOH		
	a	*b*	*b—a*	*a*	*b*	*b—a*	*a*	*b*	*b—a*
Phenolphthalein...	9.85	..	..	19.8	..	..	39.4	..	..
Litmus.....	9.75	10.5	0.75	19.8	20.8	1.0	39.9	41.5	1.6
Methylorange.....	10.4	10.85	0.45	20.8	21.6	0.8	41.4	43.2	1.8
New indicator.....	9.85	9.95	0.1	19.8	19.95	0.15	39.8	40.0	0.2

The new substance which I propose as an indicator, possesses as will be shown, an exceptionally great sensitiveness (which nearly equals that of phenolphthalein in the transition from acid to base) and can be advantageously used even with N/100 solutions.

For all the determinations normal, N/10 and N/100 solutions of sodium hydroxide, and of hydrochloric acid, adjusted with phenolphthalein were used. The new product shows its superiority to other indicators especially in the N/100 solutions. The figures in the accompanying table are the average of a great number of titrations. In order to be able to recognize clearly the beginning and end of the color change two control experiments were conducted, one in acid, the other in alkaline solution.

In the table *a* represents the number of cubic centimeters which were necessary to cause the beginning of the color change, *b* the number of cubic centimeters required to complete it. Then *b-a* represents the number of cubic centimeters during the addition of which the indicator takes on transition colors.

From these determinations the following conclusions may be drawn about the new indicator. 1. It possesses a fully satisfactory sensitiveness toward N/100 solutions. 2. The amounts of normal solution correspond to the required amounts with phenolphthalein (colorless to red) if the color change is carried out to the point of extreme coloration. These two indicators can therefore be used interchangeably. 3. Whatever concentration is used, the indicator shows practically the same sensitiveness (up to a total volume of liquid of about 80 cc.). 4. The titration can be followed out in both directions with the same exactness if it is carried out to the point of deepest color. 5. The change from deepest red to deepest violet, and vice versa, requires less normal solution than other indicators. The transition colorings are therefore confined to narrower limits than with the others.

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The Mimosa Barks and their Significance in the Leather Industry (concl.). JOHANNES PAESSLER. *Ledertechn. Rundschau*, 1910, pp. 337-8. 345-7, 354.—Eitner mentions a South American mimosa bark from Brazil, which he also calls "Bohano" bark; he finds 30-32 per cent. tannin. This bark is not a market ware.

The tannin-bearing acacia has been introduced with success in German East Africa in the mountainous regions. In Usambara, at 1,300-1,700 m. (4,000-5,500 ft.) above the sea, maturity is reached in 5 to 6 years and the yield of bark is higher than in Natal. The tannin content is high, 40-45 per cent.

The view was formerly held that Natal mimosa was poorer in tannin than the Australian bark. As the result of many analyses for years the author finds that the average is about the same from either source. Since 1901, 260 samples of mimosa bark have been analyzed at the Freiberg station with the following average (limits in parenthesis):

	Filter method	Shake method
Tans	33.0 (22-48)	31.5 (20.5-46.5)
Non-tans	9.5	11.0
Insoluble	43.0	43.0
Water	14.5	14.5

The trunk bark of the mimosa contains somewhat more tannin than that of the branches; v. Schroeder found 39.2 and 35.9 per cent. respectively. The author likewise found 33.5 and 29.6 per cent. in Australian barks.

The ratio of non-tans to tans in mimosa is considerably less than in domestic tan barks. To 100 parts of tannin there are about 30 and 35 parts non-tans according as the filter or shake methods are used. The sugar, according to v. Schroeder amounts to 3 parts which is slight compared with 26 for oak and 32 for pine. Mimosa has therefore slight acid-forming power which agrees with practice. The bark (ground) costs 22 marks per 100 k. or 0.67 and 0.70 m. per kilo of tannin (filter and shake methods). This is about equivalent to $55 per ton, and 8½ cents per pound of tannin.

Mimosa gives leather a light, somewhat reddish color which darkens by action of light. The tannin is readily soluble so that the bark can be readily extracted without leaving more than 3 to 4 per cent. of the tannin in the residue. The bark extracts well because of its fibrous structure and may yield liquors of 8 to 10 per cent. Mimosa liquors do not diminish in tannin content on standing as shown experimentally by the author in 1904. A liquor containing in 100 cc., 2.85 grams tans and 0.63 non-tans, after 60 days analyzed 2.79 and 0.41 grams, the small loss in non-tans being due to formation of volatile acids. Recent experiments at the Freiberg station have shown that mimosa has high weight-giving power, being taken up by leather in marked quantity; almost equal to quebracho. Mimosa is properly rated as adapted for sole-leather, giving a solid product. It is incorrect, however, to assume that it is unsuited for harness and upper leathers.

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The author has tanned calf-skins in pure mimosa and obtained a good full leather, soft to the touch.

Caution is necessary in employing mimosa as dusting material for lay-aways. In the first place, if there has been an insufficient fore-tannage, a dead tannage (Zugerben) results and secondly, like all materials rich in tannin, mimosa tends to produce spots when in direct contact with the hide. Mimosa should not be used in dusting the first lay-away and only gradually, mixed with other materials, in the following layers. To avoid spots, the mixture with the tannin-poor materials should be uniform. On the whole it is better not to employ mimosa for dusting, but in liquors for the handlers and lay-aways.

Commercial mimosa extracts are liquid or pasty, of density 21 to 28° B., corresponding to 63-53 per cent. water; solid extracts are not made. The average composition of the extracts is (filter method):

	Mean	Limits
Tans	31.5	27-36
Non-tans	9.5	5-12
Insoluble	1.0	0-3
Water	58.0	63-53
Mineral	1.5	1-3

The shake method gives 1 to 3 per cent. less tannin. If in the manufacture too high a temperature has been used in the extraction or unsuitable clarification, the ratio of non-tans may increase. Such a product analyzed 29 per cent. tans, 12.5 non-tans, and had a gravity of 27.5° B. High density therefore does not always imply high tannin. It dissolving mimosa extract, it is necessary to heat the water to 40-50°: the conditions are therein less favorable than with oak, chestnut or treated quebracho though better than with untreated quebracho. Very little sediment separates on cooling. The price of 1 k. tannin in extract is 84 pfennigs compared with 67 pf. in the bark. Considering the cost of extraction, and loss in the bark, it would appear best to use extract.

Extract mimosa D. manufactured according to the patents of Lepetit, Dollfus and Gansser of Milan is not a mimosa extract but sulphited quebracho. In analyses tans 38, non-tans 8 per cent. and is characterized by its high ash of 6.5 per cent.

The Valuation of Logwood. GEORG GRASSER. *Collegium*, 1910, 461-3. —The best gravimetric method is that of Schreiner which is similar to the official method of tannin determination. The total solubles in the extract are determined on evaporation, and the dyestuffs by difference on treatment with hide powder which absorbs them. The results are somewhat uncertain with varying hide powder and the method laborious. The author has therefore worked out a simple method which gives accurate enough results for valuation. The principle is to precipitate the dyestuff with lead acetate and measure the volume of the precipitate. Absolute values cannot be obtained, but various brands may be thus compared and a standard assumed. Five grams logwood are extracted

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with 200 cc. water in the author's apparatus lately described (ante, p. 526), 1½ hours sufficing. The extract is made up to 250 cc., 50 cc. of this mixture with 20 cc. of lead acetate solution (1:20) and a portion of the mixture centrifuged in a hand apparatus for 5 minutes when the settling is complete. The volume of the precipitate is not proportional to the concentration in strong solutions but the ratio becomes fairly constant when a dilution of 0.3 per cent. is reached as shown in the table.

Grams extract in 100 cc.	Cc. precipitate in 10 cc.
16	6.35
8	5.50
4	5.30
2	4.00
1	3.00
0.5	2.50
0.25	1.20
0.125	0.60
0.0625	0.30
0.0312	0.15

Since logwood averages 10 per cent. dyestuff, 4 to 6 grams should be extracted in 200 cc. for accurate work. To obtain the greatest accuracy, the standard and the sample test should be centrifuged at the same time.

The Occurrence of Osyritrin (Violaquercitrin) in Osyris Abyssinica. S. J. M. AULD. *Proc. chem. Soc.*, 1910.—A. G. Perkin separated the glucoside osyritrin from Cape Sumach (*Osyris compressa*) and showed it to be identical with viola-quercitin isolated by Mandelin from *Viola tricolor*. The author has separated the same substance from the leaves of *Osyris abyssinica* from the Transvaal. The extract from this material produced a darker and poorer leather than the Cape Sumach. The leaves contained 23 per cent. tannin. The concentrated aqueous extract was fractionally precipitated with lead acetate and the last fraction decomposed with H_2S yields a reddish brown catechol tannin. By extracting the leaves with alcohol and recrystallizing, greenish yellow crystals in needles were obtained melting at 185-6°, agreeing by analysis with the formula of osyritrin, $C_{27}H_{28}O_{16}$, $3H_2O$. On hydrolysis, it split up into a dextro-rotary sugar (osazone melting at 204-5°) and an insoluble coloring matter having all the properties of quercitin, $C_{15}H_{10}O_7$.

The Manufacture of Lacing Leather. *Ledertechn. Rundschau.*, 1910, 347-8.—For sewing and lacing leathers only large flat hides of 20 to 30 k. green weight are suited. Silesian hides are best, but even light pips may be used. When croupons (butts) are used, these are best separated after soaking, the waste going to the limes and the croupon being "geschwödet." For this, one-half k. sodium sulphide is dissolved for each croupon, of three-fourth k. for each whole hide and sufficient slaked lime added to make a thin paste. The hides are spread out flat, hair upwards, and the cold paste applied evenly with a broom. They are then folded so that the flesh is as little in contact with the liquor as possible. After one-

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fourth hour, the unhairing may begin; if by hand, rubber gloves are indispensable for protection. Washing in fresh water immediately follows, 6 hours when running, 12 hours in suspenders. After shaving and stretching the hides are again left in fresh water an equal time. If alum tanned leather is to be made, a bran bate is advisable; for colored and fat tanned leather, one-fourth hour's washing in luke-warm water is sufficient. For the alum liquor, 15 k. alum, 4 k. salt, and one-half k. wheat flour are used to 100 l. water; the bath should not be over 25° C. The first day the hides should be turned 2 to 3 times, the second day once, the liquor being stirred up each time. Old liquors may be used again when strengthened with 6 k. alum, 1½ k. salt, one-fourth k. flour to each 100 k. white hide, but should not be used more than 3 or 4 times. To tan through, 7 to 8 days are required; if complete, a thick portion of the hide when folded remains white. After drying, the leather is softened by machine or hand work, and should then be of a fine white color, mild to the touch. The greasing is done in a warm room by burning in or dipping, the fat being at 60-70° C.; the leather should first be warmed. A more practical method is to apply the grease in a drum which can be heated. The mixture is generally equal parts of stearine and tallow. For colored leathers, the dye is applied before tannage, using any water-soluble aniline dyes. The colored hides are not tanned in alum liquor, but rubbed on both sides with a mixture of 2 parts alum, 1 part salt and a little flour, then laid together in a wooden tub. Care is taken that the hides do not dry, they being turned every 2 days; the tannage is complete in 7 to 8 days.

PATENTS.

Method of Unhairing and Tanning Hides or Skins. U. S. Patent No. 976,036. GEORGE D. BURTON, Boston, Mass.

The hides are placed in a solution of sal soda, and an electric current is then passed through, intermittently, the solution being kept agitated. This process removes the fat from the hides. They are then taken out and fleshed and washed in a weak acid solution. They are then placed in a tanning solution and again subjected to the action of electric current.

Process of Electrolytically Treating Tannic Infusions of Plants. U. S. Patent No. 975,835. H. DAMKÖHLER AND H. SCHWINDT, Bremen, Germany.

Leather-Working Machine. U. S. Patent No. 975,628. GEORGE MCKEEN, Peabody, Mass.

Pressure Device for Leather-Skiving Machines. U. S. Patent No. 975,495. CHARLES H. BAYLEY, Boston, and BENJAMIN F. MAYO, Salem, Mass., assignors to United Shoe Machinery Co.

Leather-Wringing Machine. U. S. Patent No. 976,968. ROBERT F. WHITNEY, Winchester, Mass.

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Method of Manufacturing Substitutes for Leather-Board. U. S. Patent No. 976,827. A. J. OSTBERG, Australia.

The method consists in cutting leather scrap into thin shavings and then mixing them with some adhesive and subjecting them to pressure.

Table for Leather-Working Machines. U. S. Patent No. 978,120. E. Y. B. ENGELMAN, NOXEN, PA.

Formic Acid. U. S. Patent No. 975,866. HENRY HOWARD, Boston, Mass.

Sulphur trioxide in gaseous form is passed into water containing a formate.

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Journal of the

American Leather Chemists Association

Vol. VI FEBRUARY, 1911 No. 2

W. K. ALSOP . . . . . Editor and Manager
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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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A SUGGESTION FOR COLLABORATIVE WORK ON COLOR VALUATION.

By W. S. Loud.

During the past few years I have been particularly interested in the work of the Association in respect to color tests, especially concerning those employing pelt, and I believe that it is possible for these tests to be of much more practicable use than at present. The man experienced in handling leather undoubtedly prefers the tanned hide as a medium of comparison of color valuation and probably those of us who advocate so strenuously the color measurement method would resort to the pelt to really *know* something concerning the extract with which we are working.

I think it is because of the fact that a good piece of leather really *proves something* that a method involving color measurement as a valuation is not always desirable. I have seen extracts which were apparently all right by the analysis, but color tests proved them worthless; had we used the tintometer or cloth method instead of pelt these extracts might have caused considerable trouble.

A color test made on sheep skiver should have a thickness of at least one thirty-second of an inch when finished, in order that it may be worthy the name of leather and also because of the fact that skins of this sort can be stretched but very little; thus the color imparted to the pelt by the tannin remains. Color tests made on very thin skivers can be stretched and worked until the resulting color is many shades lighter than the original. Many of the color tests accompanying reports at the present time are thin nearly to the degree of transparency.

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We have tried to work out a scheme of processing heavy sheep skivers by which comparative results can be obtained, and think, in so far as our own laboratory is concerned that the results have been very good, although it is only possible to determine the practical value of the method by collaborative work. For this reason we would like to get results from other chemists who might desire to process skivers according to the following scheme.

If a laboratory is making color tests every day, and a bottle drum holding two gallons is available, eight hundred grams of the heavy skivers (pickled weight) cut in pieces four inches square may be processed at one time, as they will keep in good condition for three months or longer. After weighing the skins cut up for washing, place under the tap in a screen and wash for one-half hour, wring well, and drum in distilled water at 90° F. for fifteen minutes. Rinse well under the tap, drum for ten minutes, wring and place in a solution containing borax equal to 10 per cent. of the pickled weight of the skivers. Drum this solution for eight hours, wash thoroughly under tap, drum twice for twenty minute periods in distilled water at 90° F. Wring and rinse after each operation and then drum in a solution containing one per cent. of acetic acid based on the pickled weight. Drum for one-half hour and keep skivers in a glass stoppered jar.

In this slightly acid solution the skins will keep for an indefinite period and require no washing previous to tanning, as the small amount of acetic acid present does not seem to influence the color of the finished test. Skins preserved by this treatment are much superior to those kept in borophenol or formaldehyde, as the acetic acid plumps but little and keeps them in a soft and pliable condition for tanning.

The procedure is somewhat tedious, but because of the fact that so many can be treated at one time, together with the fact that the skins will keep well, there is undoubtedly a great saving of time over a method involving washing or preparing the skins each day.

I believe that interesting results would be obtained if collaborative work were done on the method as outlined above.

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ACIDS IN TAN LIQUORS.[1]

By Prof. H. R. Procter and A. Seymour-Jones.

The present great interest in the subject of this paper, as shown in the recent conference of the I. A. L. T. C., has rendered its early publication desirable, a fact which we somewhat regret since the recent important paper of Sörensen on "Enzymes" bears largely on a similar subject. In the present paper we have devoted much attention to indicators, and have had necessarily to accept certain of the views of other chemists who have worked on this subject; and Sörensen's work promises to throw fresh light on many points that we had regarded as settled. As we have as yet had insufficient time to digest his work and none to perform further experiments, much that follows must be regarded as more or less provisional.

For the past twenty-five years the question of the acidity of tan-liquors has been prominent in the chemistry of leather manufacture, and during that period upwards of twelve methods have been devised to estimate it, none of which have proved wholly satisfactory. On the other hand, the effect of the acids on the absorption of tannin by the skin and the rôle which they play in the production of sound leather, has only been studied empirically by practical tanners, and has received no attention from the research chemist.

It therefore seemed advisable to study both these questions; but in the present paper, we only propose to give an account of our work on the estimation of the acidity of tan liquors, leaving the study of its effects to a later publication. As the whole question largely depends on facts in physical chemistry which are of somewhat recent elucidation, it may be well to preface the account of experimental work by some remarks of a theoretical character.

The distinction has long been made in practice between "strong" and "weak" acids, without any very clear conception of the nature of the difference. Equal molecular quantities of either will neutralize or saturate equal quantities of base; but if a "strong" acid, such as hydrochloric, is added in excess to the salt of a weak acid such as acetic or carbonic, the weak acid

[1] *Journal of the Society of Chemical Industry*, December 15, 1910.

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is liberated and the strong takes its place in the salt. Corresponding to this, salts of strong bases with weak acids often exhibit in solution marked alkaline properties, though chemically neutral (*e.g.*, sodium carbonate). The acid "strong" in this sense does not become "weak" by dilution with water, but rather the "weak" acid when diluted approaches the properties of the "strong" acid of the same concentration.

While the alkali-saturating power of all acids of equivalent molecular concentration is the same, their other effects are often widely different, and though their swelling effect on hide cannot be said to vary directly with their "strength," it is yet closely connected with it, and acids of a very weak character have no appreciable swelling power, though they still neutralize lime. As to the nature of "strength" and "weakness," the following may be stated. All acids may be regarded as compounds of the hydrion H′ and an anion or acid forming group, and all alkalis as hydroxyl, OH, and a kation or basic group. When the two are brought together the H and OH unite to form water, while the anion and kation constitute the salt. The more loosely the hydrogen is held and the more readily it reacts, the stronger the acid is; and the same holds of a base with regard to its hydroxyl. In modern chemical theory the strong acid is supposed in dilute solution to be already almost wholly separated (ionized) into hydrion (the single H′) and anion, while in the weak, only a small proportion, which, however, increases with increasing dilution is so dissociated. Whether this percentage of ionization is actual, or only represents a certain average freedom, is unimportant—it is at least a convenient numerical way of stating what in some sense or other is an established fact.

The strength of an acid is therefore dependent on the amount of hydrogen ions in a given volume of the solution, or, in other words, on the hydrion concentration of that solution. Just as we measure the concentration of an acid or an alkaline solution in normal, decinormal, centinormal, etc., so we measure the hydrion concentration in the same way. A normal solution of hydrion would contain one gram molecule of hydrogen ions per liter, and such a solution would correspond approximately to a 1.35 normal hydrochloric acid solution.

We have thus two meanings for the strength of an acid solu-

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tion, firstly the total molecular quantity of acid which it contains, *i.e.*, its value as measured by the quantity of "normal" alkali required to saturate it; and secondly its acid strength as measured by its sourness and other "acid" properties, and more strictly by its hydrion concentration. In the case of N/10 HCl. these two quantities are nearly the same, since almost all the acid hydrogen is present as free hydrions; while in an N/10 solution of gallic acid they are extremely different, as nearly the whole of the hydrogen remains attached to its anion, and the solution is not perceptibly sour. If, however, caustic soda is added, the small percentage of free hydrions unite at once with its hydroxyls to form water; more hydrions are evolved from the undissociated acid to take their place, and in turn are used up. The hydrogen ions which thus remain in reserve in the undissociated acid molecule are known as "potential" hydrogen ions. In the end the whole of these are combined to form water and the soda is neutralized; though at no time has the solution been more than feebly acid. The importance to the tanner of this difference of behavior is obvious, since by the use of a chemically weak acid he is able to neutralize lime and other bases in the hide without producing undesirable swelling, while on the other hand for swelling purposes the acid employed must have a certain concentration of free hydrions. In discussing the very great dilutions which have to be considered in some cases, it is to be remembered that water itself is not wholly devoid of acid and basic properties, but contains free hydrions and free hydroxyl ions in equal quantities and each to the extent of about 10^{-7} normal (N/10,000,000). Therefore in neutralizing an acid the point of true neutrality is not 0 as might be supposed, but 10^{-7} normal; even alkaline solutions contain free hydrions, though balanced by larger amounts of free hydroxyl ions.

As before indicated, we may directly determine the "acidity" in two ways; the first method is to measure the "actual" hydrion concentration; the second, to determine both "actual" and "potential" hydrogen ions by direct titration. In the latter we have to use indicators, and with regard to these there are certain points which technical chemists often fail to realize. Firstly, the color change of the large majority of indicators is grad-

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ual, extending over a considerable range, although between definite limits of hydrion concentration, which vary with the nature of the indicator. Phenolphthalein has a fairly sharp color-change at 10^{-8} to 10^{-9} normal hydrion concentration, while methyl orange has a gradual color change extending from 10^{-3} to 10^{-5} normal. In the light of these facts the discussion of haematein later in the paper should prove interesting.

It should now be obvious that as different indicators change their distinctive property, color or other characteristic, at definite though different hydrion concentrations, varying amounts of strong and weak acids will be estimated according to the indicator used. This raises an interesting point, as some chemists lay great stress on the "accuracy" of a method; that is to say that they take an artificially acidified liquor and endeavor to estimate the same amount of acid as that put in. Let us suppose that to 95 cc. of a neutral solution of tannin they have added 5 cc. N/1 acid, this latter having been prepared by standardization against N/1 alkali and phenolphthalein, the color-change of the latter taking place at 10^{-8} normal hydrion concentration. In estimating the acidity of this liquor unless the color-change of the indicator used takes place at the same hydrion concentration as phenolphthalein, the amount of acid estimated will always differ from the amount originally added, by amounts varying with the strength of the acid used and the neutral salts of weak acids present. Thus the search after a method which will estimate the same amount of acid as that put in, is futile so long as the indicators are mixed and the relationship between them is not specified.

One other point requires discussion before proceeding to a consideration of the work accomplished, viz., the effect of extensive dilution of the acid solution. It can easily be seen that dilution with water would, in most cases, affect the hydrion concentration. If all the acid were not dissociated then addition of water would cause a certain number of "potential" ions to be converted into "actual" ions, while if the acid were wholly ionized then addition of water would decrease the hydrion concentration. Thus if to an acid solution which has a hydrion concentration of 10^{-4} normal, *i.e.*, just sufficient to turn congo red blue, we add water until the hydrion concentration has fallen

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to 10^{-5} normal, the solution will no longer affect congo red. Thus dilution of an acid solution always tends to alter the amount of acid estimated, and is in most cases highly undesirable.

Under the same heading we may speak of the effect of the presence of neutral salts on the hydrion concentration. It must be accepted by the layman as a fact that the presence of neutral salts, especially those which have an ion in common with the acid (*e.g.*, sodium acetate and acetic acid) always tends to prevent the dissociation of an acid into its ions, and while the determinable acidity of such a solution may still be high, the actual hydrion concentration may fall very low.

The first step in our experimental work was the examination of the published methods for estimating the acidity of tan liquors. All these methods were carried out in their most recent published details. *Procter's lime-water method* depends on the principle that tannin and many allied phenolic bodies form insoluble calcium (or possibly lime) salts on the addition of a clear saturated solution of calcium hydroxide to the liquor, while the organic acids usually present in the liquors form soluble calcium salts. In this way is determined the actual "lime dissolving" power of the liquor, and an important piece of information conveyed to the tanner.

In Procter's Textbook of Tanning the following passage occurs: "A liquor may have acidity equal to several cc. of lime-water and yet react absolutely alkaline to methyl orange. Hence the acidity of a liquor available for plumping may be taken as represented by the lime-water required to change the red of methyl orange to yellow, and if the liquor does not redden methyl orange then it is incapable of plumping."

These words were written thirty years ago, and we can now show them to be perfectly true. Methyl orange changes color at a hydrion concentration of 10^{-4} normal, and although solutions of about 10^{-5} normal showed a slight tendency to plump, it was found that the limit might be more correctly fixed between 10^{-4} and 10^{-5} while that of the lime-water method is nearer 10^{-6}.

Theoretically the lime-water method is good as it involves no detannization or dilution of the liquor, but it has to be used very carefully to give concordant results, and apparently the

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experiences of the American leather chemists with it have been far from happy ones. They state that with tail liquors which contained very little tannin no end point was obtainable as only a darkening of the liquor took place without any turbidity. This difficulty could no doubt have been overcome by the addition of some neutral tannin solution as indicator, though it may be remarked in parenthesis that absolutely neutral tannin solutions, especially of the pyrogallol variety, are difficult to obtain. The presence of acids giving insoluble lime salts in acid solution, such as oxalates may be met by the addition of some calcium chloride before filtration.

The real objection to the method lies in the uncertainty of the indicator, viz., the insoluble calcium tannin compounds. This involves two main defects, since certain tannins give somewhat soluble lime salts, and some organic calcium salts are insoluble; and secondly, the indefiniteness of the end point. It is not easy to obtain exact concordance between two observers, for difference of opinion nearly always exists as to what constitutes "a trace of turbidity," which marks the commencement of the formation of the calcium tannin compounds. The results of five observers are given in cc. of saturated lime-water per 10 cc. of liquor:—

Observer	1	2	3	4	5
Liquor X	14.7	14.9	14.6	15.05	15.0
Liquor Y	11.6	12.0	11.7	12.1	11.8

Fifteen readings taken by one observer on two favorable liquors at intervals of five minutes were as follows:—

Liquor X	14.7	14.65	14.65	14.7	14.6	14.7 all others	14.7 cc.
Liquor Y	11.6	11.6	11.5	11.55	11.5	11.65 "	11.6 cc.

Abnormal liquors were, however, examined, which did not yield such concordance. For example, a very dark, strong handler liquor was examined and, though filtered clear, five titrations had to be made before concordance to 0.3 cc. could be obtained. More concordant results could be obtained by dilution of the liquor with distilled water, though as has been stated dilution is never desirable. It is, however, apparent that if the observer and the concentration of the lime-water be kept constant, and if trouble be taken to obtain brilliantly clear filtrates

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and with the aid of printed matter underneath the titration vessel, the method is useful for all practical purposes.

The method of Kohnstein and Simand (Ding. Polyt. Jour., 1885, cclvi. pp. 38, 84) depends on the treatment of the tan-liquor with magnesia free from carbonate and lime, and upon the difference in solubility of the magnesium salts subsequently formed, and only estimates those acids with soluble magnesium salts, and if a tannin chances to have a soluble magnesium salt then that tannin will be estimated as an acid.

This method is very laborious, and we have been unable to obtain the accuracy and concordance which have been claimed for it. The following are the results of experiments on six liquors, stated in grams of acetic acid per liter. Although the various sub-divisions of the method were carried out only the total acid results are given, as their accuracy did not seem to justify further detail.

	First titration	Second titration	Third titration
Liquor 1	0.0477	0.0504	0.0450
Liquor 2	0.0292	0.0346	0.0308
Liquor 3	0.1471	0.1393	0.1309
Liquor 4	0.3684	0.3418	0.3777
Liquor 5	1.4518	1.5822	1.5200
Liquor 6	3.8670	3.0920	4.4878

A defect pointed out by Bennett and Wilkinson (this J., 1907, 1186) was confirmed by the present experiments, viz., the inconstancy of composition of some of the magnesium compounds with organic acids, excess of magnesia forming basic salts. A theoretical advantage of the method is that it involves no dilution of the liquor, but in the author's opinion it is too elaborate and too little reliable for general use.

A method suggested by Bennett and Wilkinson in this Journal (*loc cit.*) involves the use of lead oxide (litharge) both as a precipitant for tannin and as an absorbent for acids, only those acids with soluble lead salts being estimated.

The details of this method as laid down in the J. S. C. I. were most carefully carried out, but it does not appear that lead oxide is a satisfactory means of differentiating acids and tannins, and the compounds formed with both are apparently of irregular composition and uncertain solubility. Results obtained with the

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method show that lead salts of the acids are formed of varying range of basicity, and this seriously affects the final estimation.

A comparison of the above method with the lime-water method is interesting. Results are given in grams acetic acid per liter:—

	Liquor A	Liquor B	Liquor C	Liquor D
Lime-water method	1.34	1.50	3.63	2.44
Bennett & Wilkinson	2.17	1.62	2.41	1.98

The method published by Koch (Ding. Polyt. Jour. 1887, page 395) and subsequently modified by Paessler & Spanjer (*Collegium,* 1903, pp. 10 and 17) depends on the removal of tannin by precipitation with a 0.2 per cent. aqueous gelatine solution, and subsequent titration of the supernatant liquor with standard alkali and an indicator. The method which has been largely adopted, was very thoroughly examined with no very satisfactory results. Theoretically azo-litmin should be a good indicator for the purpose, as its main color change takes place at a hydrion concentration of 10^{---8} normal, which includes most bodies with any claim to acidic properties, but the color change is gradual and the end point difficult to determine, so that the personal equation enters largely, and concordance between observers is not usually good. Examples are given of six liquors and five observers. Results in cc. N/10 alkali for 25 cc. liquor:—

Observer	1	2	3	4	5	
	cc.	cc.	cc.	cc.	cc.	
Liquor A	19.4	19.1	19.3	19.8	19 4	N/10 alkali
Liquor B	21.7	21.2	21.45	22.1	21.3	"
Liquor C.....	15.9	15.0	15.9	15.5	15.15	"
Liquor D	17.3	17.1	17.8	17.4	17.9	"
Liquor E	17.0	16.8	17.4	16.5	16 9	"
Liquor F	24.55	24.0	24.1	23.8	24.4	"

A very serious objection may be advanced against nearly all methods involving detannization, *i.e.,* that certain amount of acid is co-precipitated with the tannin. It will be shown later that in every case of detannization so far examined varying amounts of the bodies otherwise estimated as acids are carried down with the tannin.

Another objection to the method is that even an experienced observer usually has to make about five titrations before concordant results can be obtained.

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Results in cc. N/10 KOH for 25 cc. One observer:—

	Results in cc. N/10 KOH for 25 cc. One observer. Liquor A cc.	Liquor B cc.	Liquor C cc.
1st titration	21.1	23.4	12.7
2d titration	20.6	22.8	12.1
3d titration	20.2	22.6	12.1
4th titration	20.0	22.45	12.0
5th titration	20.0	22.40	12.0

A zinc oxide and hide powder method proposed by the commission (A. L. C. A. Jour., 1906, p. 223) appointed by the American Leather Chemists Association was carefully examined, though without much hope of good results.

The working details were the following:—

Sixty cc. of the liquor were diluted to one liter. To 200 cc. of this solution 20 grams of moist hide powder and one teaspoonful of chemically pure zinc oxide were added. These were shaken in a shake machine for five minutes and then filtered; 100 cc. of the filtrate were titrated with decinormal alkali in the presence of phenolphthalein, adding a little zinc oxide to give a sharper end reaction. The requisite correction was made for moisture in the hide powder, and a blank sample run to determine free acid in the latter.

The results obtained were not concordant, and in every case were much lower than with any other method. This was due not only to the fact that hide powder very readily absorbs acids, but that zinc oxide combines with most acids to form neutral salts.

A few corrected results are compared with the lime-water method below, the results of the latter having been calculated into cc. N/10 alkali.

Liquor	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	
ZnO + hide powder	10.9	12.7	12.5	8.8	9.8	N/10 alkali
Lime-water	15.4	16.1	16.8	12.4	10.3	"

For some years past the American Chemists Association has been particularly persevering in its endeavors to find an accurate and concordant method for the estimation of acidity of tan liquors. The charcoal method of Simand was first of all adopted as official. This method consists in detannizing a measured volume of the liquor by animal charcoal, and estimating the acidity of the remaining solution by titration.

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Although the animal charcoal used was labeled C. P., we found it an altogether unsatisfactory agent for the removal of tannin and coloring matters in the presence of acid. Very varying results were obtained and a number of blank experiments showed that the errors were due to the unequal amounts of acid absorbed by the animal charcoal together with the tannin; varying in six blank experiments from four to fourteen per cent. of the total acid. This serious defect has also come under the notice of the American chemists, who universally condemn the method.

In 1906, A. W. Hoppenstedt tried to solve the problem by removing the tannin by means of an alcoholic solution of quinine, and then titrating the filtrate consisting of the quinine salts of the acids with caustic alkali in the presence of phenolphthalein. (J. A. L. C. A. for September, 1907.) In experiments carried out in this way the precipitation of quinine and tannin filtered well, but on titration the dense precipitation of the liberated base considerably masked the end reaction. This could, however, be remedied by a number of titrations. Instead of titrating 100 cc. of the filtrate it was found more convenient to work with smaller volumes, and more concordant results were obtained by titrating 20 cc. of the filtrate at a time. The following figures show the concordance of the method:—

	cc.	cc.	cc.	cc.	cc.
Liquor A	31.3	31.2	31.2	31.2	31.25 N/10 KOH
Liquor B	28.4	28.3	28.2	28.25	28.3 per 20 c.c.
Liquor C	24.9	24.8	24.7	24.8	24.75 liquor.
Liquor D	10.7	10.5	10.35	10.55	10.2

Although the method involves detannization and considerable dilution of the liquor, both of which tend to lower the results, it gives higher results than most other methods; although quinine co-precipitates quite an appreciable percentage of acid. This fact is probably due to the production of weak acids by oxidation, and the use of phenolphthalein, which estimates many bodies of very feebly acid properties.

Comparison was made between this method and a direct titration with N/10 alkali and phenolphthalein paper, working in an atmosphere of coal gas to avoid oxidation of the liquor:—

Liquor	1	2	3	4
Detannized	31.2	28.3	24.8	27.7
Undetannized	31.75	28.5	25.1	27.9

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The method has to be worked quickly and the filtration must be very rapid to prevent oxidation and darkening of the filtrate. This renders the method awkward to manipulate, and an undesirable and laborious condition, in which a considerable error is possibly introduced, is the necessity of making yard liquors up to the same strength as that used in tannin analysis.

Phelan and Fiske have suggested a means (J. A. L. C. A., 1908, pp. 99) whereby the method ordinarily employed to determine CO_2 in carbonates is so modified as to be available for determining the acidity of tan liquors. A definite volume of liquor is mixed with calcium carbonate, the carbon dioxide driven off, dried, and collected in U tubes containing soda lime. The increase in weight of the tubes is taken as proportional to the amount of acid in the original liquor. In this case only those acids which, at boiling temperature, will liberate carbon dioxide from calcium carbonate are estimated. The method is ingenious, but requires a somewhat elaborate apparatus and is quite as laborious as the Kohnstein-Simand, neither the additional labor nor the additional apparatus being justified by accuracy or concordance of results. It should be stated that a similar apparatus was given an extended trial at Leeds some years prior to the above publication and did not prove successful.

In the J. A. L. C. A. for March, 1908, p. 85, Reed describes two new methods for the estimation of acids in tan liquors based on the precipitation of tannin by an alcoholic solution of gelatine, and subsequent titration of the filtrate from the tanno-gelatine precipitation with standard alkali, using an alcoholic solution of haematein as indicator. In the second method he merely modifies the first by substituting a basic dye for the alcoholic gelatine solution, and titrating the solution as before in the presence of the same indicator.

Both these modifications were thoroughly investigated, and the first as a practical works control method is certainly good; the second method is in no way promising. As indicator a pure sample of haematein was obtained from the University Tinctorial Chemistry Department, of which a fresh solution had to be prepared each day, as haematein in solution rapidly undergoes change.

In his original paper, among other observations, the author

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makes the following:—"It is not necessary that the supernatant solution from the tanno-gelatine precipitation should be clear, nor is it imperative that there should be an entire absence of tannin in the solution, as haematein is practically neutral to tannin." Reed also states that "where a water solution of gelatine or salted solution of gelatine was used, a much bulkier precipitation was obtained and an appreciable loss of acid resulted. When alcohol is used there is perhaps a trifling loss of acid. It was observed that the alcoholic gelatine solutions gave a better precipitation on standing than when freshly made." He also admits that a correct end point determination with haematein requires much practice, and trusts "that the method will not be condemned if the analyst fails immediately to make successful determinations." It is also noted that "haematein is affected to a much less degree by salts of gallic acid in the presence of alkalies than is phenolphthalein. In the titration of acetic, lactic, and gallic acids and their mixtures, it will give with standard alkali practically the same calculated acid as will phenolphthalein, perhaps a shade less as it is more susceptible to alkalies." These statements may be confirmed and the method was found convenient to work and gave fairly concordant results, combined with rapidity of execution, but the end point with haematein is never easy to determine. The best results obtained were:—

Titration	1	2	3	4
Liquid A	10.7	10.65	10.6	10.5
Liquid B	15.2	15.2	15.25	15.25
Liquid C	15.6	15.5	15.45	15.45
Liquid D	20.9	20.8	20.8	20.8
Liquid E	17.55	17.40	17.35	17.40
Liquid F	21.4	20.9	20.5	20.2

Results are given in cc. N/10 KOH required for 25 cc. of liquor.

Liquors A, B, C, D, and E, represent the best results and F one of the worst, and the method is open to one or two objections. Detannization with alcoholic gelatine solution is little, if any, more advantageous than that with aqueous gelatine, in so far as the extent of the co-precipitation of acid is concerned, but filtration is much easier since the precipitate is less bulky and more compact, probably because of the dehydrating power of the alcohol. A second difficulty is the character of the indi-

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cator used. While other indicators change color more or less sharply at a definite hydrion concentration, haematein is practically always changing color from a hydrion concentration of twice normal (= 6.034 × N/1HCl) to 10^{-15} normal (= 6.8 × N/1KOH), but the authors estimate that the particular color change taken as end point by them took place at about 10^{-7} normal. The question of the haematein indicator is gone into more fully later, but the following is a comparison of two observers using the gelatine haematein method on five liquors:—

Liquor	1	2	3	4	5
Observer 1	10.65	15.2	15.6	20.9	17.45
Observer 2	10.8	15.6	15.85	21.2	17.7

The basic dyes recommended in Reed's second method are lemon-yellow "O" (sold by the Berlin Aniline Works), thioflavine F, methyl violet, and auramine. Only the latter pair were tried by the present authors, but the precipitation of tannin seemed very imperfect. Clear liquids were never obtained by a single filtration and were always highly colored, which absolutely precluded the use of haematein as an internal indicator.

In the J. A. L. C. A. for June, 1910, Yocum and others propose a modification of the gelatine haematein method by removing gallic acid by precipitation with gelatine in the presence of gum arabic. They state that the one serious defect of the original method is that it includes the non-plumping acids in the estimation, and where a large proportion of the tanning materials used are of the pyrogallol variety, the amount of gallic acid thus estimated is very considerable.

Experiments show, however, that the reaction is by no means a quantitative one, and considerable amounts of gallic acid are found in the liquor after treatment; while gum arabic itself is usually quite acid in solution. A much more convenient and scientific method is to select an indicator such as congo red paper, which is not sensitive to hydrogen-ion concentrations too weak to plump.

Haematein is scarcely affected by tannins, and if the titration is conducted under petroleum ether as described in a subsequent part of this paper, and the liquid spotted on haematein paper freshly blued by very dilute ammonia, well washed, and

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used on a tile in a moist condition, very good results are obtained, though it is still not easy to fix on a definite end point.

An incomplete and unpublished method by Procter and Law consisted in the direct titration of the unfiltered and undetannized liquor with N/10 NaOH, using haematein paper as an external indicator.

Probably the best method for detannization which was examined, was that of Stiasny, which involves the precipitation of the tannin by formaldehyde in the presence of hydrochloric acid, but is unfortunately restricted to the catechol tans, which alone are completely precipitated. The details of the estimation were as follows:—

Twenty-five cc. of the tan liquor were pipetted into a flask, 20 cc. of N/2 HCl and then 10 cc. of carefully neutralized formaldehyde were added, and the whole boiled with a reflux condenser for ten minutes. The whole of the tanning and coloring matters were precipitated, leaving the 20 cc. N/2 HCl and the unknown quantity of acid in a brilliantly clear solution. The flask was rapidly cooled under the tap, the solution filtered, and the precipitate well washed. The filtrate and washings were then titrated with N/2 KOH and phenolpthalein, when any cc. of N/2 KOH above the 20 cc. required to neutralize the HCl added, represented the acid previously present in the liquor.

This method was thoroughly tested on quebracho, mimosa and gambier liquors. It was shown that in this case, owing possibly to the unusual character of the tannin precipitation, very little co-precipitation took place. The results were somewhat high, as the indicator used was phenolphthalein. It was found convenient instead of performing the whole titration with N/2 KOH, to add 20 cc. of the latter to neutralize the 20 cc. of N/2 KOH, and then titrate with N/10 KOH. Unfortunately the reaction with pyrogallol tans is neither complete nor quantitative.

A method which was formerly in use at the Vienna research station, though not tested in the present work, is interesting in that while theoretically wrong, it gave in many cases fair practical results. The principle of the method was to run into the acid liquor excess of standard caustic soda, and then utilize the excess of soda to liberate ammonia from ammonium sulphate,

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the gas being collected in standard acid in the usual way. This of course would enable the operator to calculate the concentration of acid in the original liquor.

We have not had time to examine the complicated method and apparatus of Georg Grasser (*Collegium,* October, 1910, p. 406), but many difficulties and at least theoretical objections present themselves to anyone familiar with the problem, and in the final estimation of non-volatile acids it relies on the method of Koch, which we have already criticized. With regard to volatile acids, we need only point out as a well-known fact, that in steam distillation considerable quantities of lactic acid are invariably carried over with the acetic.

This completes the list of published methods. It will be seen that the great difficulty lies in the fact that a tan-liquor may contain any acid from strong acids like formic to phenolic bodies with feebly acid functions, and that if we estimate the acidity by titration with an alkali we always have to make an arbitrary choice of the end point by specifying a certain indicator. Thus no one method can give the tanner all the information he requires. If he wants to know the lime dissolving power of his liquors, probably nothing can give it better or more directly than the lime-water method. If he requires the actual present acidity of his liquor it can only be given in the form of the hydrion concentration, but this point will be discussed later. If he requires the total acid, he must, by choice of a suitable indicator, decide at what point he will draw the line between acid and non-acid bodies. Phenolphthalein, for instance, will include not only all trade acids, but some substances which are really not acids at all, though they have a feeble power of combining with bases; while methyl orange or congo red exclude many of the weaker true acids. It must also be remembered that in presence of the excess of alkali, which is required to influence such indicators as phenolphthalein, many really neutral bodies are hydrolyzed to bodies of a more acid character, as for instance tannin to gallic acid; and in the presence of oxygen still more profound changes take place, mostly in the direction of increased acidity.

Several of the methods which have been described involve the previous detannization of the liquor, and it has been pointed out that this in almost all cases is accompanied by marked co-

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precipitation of acid. A rather considerable series of experiments was therefore made to test the effect of different methods of detannization, using throughout each series the same indicator. In each case 25 cc. of the liquor was titrated under petroleum ether to avoid oxidation, and the figures given are the number of cc. of N/10 KOH required for neutralization. To prevent or lessen oxidation, petroleum ether was used as described in a later part of the paper.

Series I.

Indicator	Moist haematein paper				
Liquor	A	B	C	D	E
Strength (grs. tan.)	0.70	1.5	2.3	2.8	3.04
Gelatine, aqueous	16.4	15.5	10.9	18.7	19.4
Gelatine, alcoholic	16.2	15.7	10.8	19.05	19.6
ZnO and HP	14.3	14.1	8.2	15.6	16.55
No detannization	16.7	16.05	11.1	19.2	19.85

Series II.

Detannization with gelatine salt solution as used in the Loewenthal method. Indicator moist haematein paper:—

Liquor	Before detannization	After detannization
Handler A	14.45	13.9
Handler B	16.05	15.6
Gallotannic	6.7	6.4
Mixed mimosa	10.3	10.1
Quebracho	10.05	9.6
Mixed liquor	11.3	11.05
Light leather suspenders	16.5	16.05

Series III.

Comparison of the Stiasny formaldehyde method of detannization of catechol tanning liquors with the Simand animal charcoal method:—

Indicator—Phenolphthalein paper.

Liquor	Stiasny cc.	Simand cc.	No detannization cc.	
Quebracho	10.70	10.40	10.65	N/10 KOH
Mimosa	7.45	7.30	7.45	"
Gambier	14.1	13.75	14.0	"
Mixed catechol	9.9	9.70	10.0	"
Mimosa	10.95	10.7	10.95	"

It will be seen from these results that in every case except Stiasny's method, detannization lowers acidity, through mostly

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not to a serious extent for works control. The tannins themselves are either non-acid, or of such feeble acidity that for practical purposes it may be disregarded, and it is not difficult to choose indicators on which they have no observable effect, so that probably the most accurate results are obtained by direct titration without detannization, but with a suitable indicator. We have therefore made a somewhat detailed study of the possible indicators, not merely as regards the possibility of a rapid and accurate estimation of the total acid, but with a view of determining the proportion of acids of different "strengths;" and while our efforts to find ideal indicators have not been wholly successful, details of our results are given, in the hope that they may at least save others from useless investigation.

Since rapidity and ease of execution is often of equal importance to extreme accuracy in technical work, it is clear that a liquid internal indicator would present considerable advantages, but in most cases this is precluded from the dark color of the undetannized liquor, and resort must be had to the less satisfactory spotting on paper, which, however, often obviates the necessity of a somewhat tedious filtration. On the whole the greatest difficulties arise from the slow color-change of most indicators which renders it difficult to fix a precise end point recognizable by all operators.

It is well known that gallotannic acid and all other pyrogallol tannins hydrolyze or oxidize rapidly in alkaline solution in contact with air or oxygen to form increased quantities of acid. Consequently when an acid pyrogallol tannin solution is slowly titrated without any precautions to exclude oxidation, the value obtained is much higher than with a rapid titration; and in fact, within limits, the slower the titration the greater the amount of acid estimated. The precautions taken to prevent this have been mentioned, but it may be of interest to give a short account of the work carried out to obviate this difficulty.

In a good many preliminary experiments we attempted to obtain a neutral atmosphere inside the titration flask by bubbling coal gas through the liquor. This had the advantage that the reducing action of the coal gas to some extent counteracted the oxidizing action of the alkali, and gave quite satisfactory results, but the use of coal gas is objectionable owing to its ex-

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plosive properties when mixed with air. Petrol ether, boiling below 40° C., which is a neutral liquid with a heavy vapor and sufficiently volatile to produce a neutral atmosphere on agitation, was tried with great success, and a further modification was introduced by the use of a small separating funnel. Into this was run the liquor to be titrated (usually 25 cc.), 2 cc. of the petrol ether were added, forming a layer over the oxidizable liquid, and by judicious agitation the vapor could be made to rarefy the air in the funnel to a considerable extent. The tan liquor was now titrated by dropping the standard alkali through the layer of petrol ether, and vigorously shaking to ensure thorough mixing and the maintenance of a neutral atmosphere. The tube of the separating funnel was cut off just below the tap, so that after each addition of alkali one drop of the liquor could be withdrawn and spotted on the paper indicator. This method was very effective in preventing any rapid oxidation. When the titration was finished and the reading had been taken, the tan liquor was run out from the bottom of the funnel, and the petrol ether left, where, if required it could be thoroughly washed in the funnel with water, and used again.

This method was used on all the following indicator tests:—

Mauvein was found to be only sensitive to acids above decinormal in strength, and was consequently useless for the purpose in view.

Methyl violet did not prove at all useful as the color-change was very gradual, and the only distinct change from blue to violet took place at a hydrion concentration of 10^{-2} normal.

Benzopurpurin has too gradual a color-change, allowing of differences up to 5 per cent.

Congo Red changes color from violet to scarlet at 10^{-4} normal, and as paper is quite the best indicator for this acid concentration. The paper is kept in the red (alkaline) state, as this is the most stable. This indicator may well be used by the separating funnel method to estimate the plumping acids of any liquor. Readings can usually be obtained to 0.1 cc.; it can conveniently be used in conjunction with some indicator of a later color-change to estimate both strong and weaker acids. Sörensen has found that congo red, being a colloidal indicator will not estimate acids in the presence of proteid matter. As we

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propose to use the indicator in the form of test paper, by which the congo red is already strongly adsorbed, we believe that this difficulty will be obviated.

Methyl Orange changes color at a hydrion concentration at 10^{-4} normal, and is quite serviceable in the form of paper. It gives approximately the same end point as congo red, but the color-change is not so pronounced, though the results obtained showed excellent concordance.

Gallein is useless as an internal indicator for liquors, and in paper the color-change is not sufficiently definite.

Sodium Alizarin monosulphonate has a rapid color-change at 10^{-5} normal hydrion concentration, and proved fairly useful as paper. It was not so good as congo red or methyl orange for ordinary work but proved very serviceable in the approximate estimation of the actual hydrion concentration.

Carminic and Rosolic acids in pure acid and alkaline solutions have sharp but delicate color changes at 10^{-5} and 10^{-7} normal respectively. The delicacy of the color changes was such as to render it impossible to use the indicators either internally or as paper.

Lime-water. The advantages and disadvantages of using the action of lime water on tannin as an indicator have been discussed.

Lacmoid changes color at a hydrion concentration of 10^{-6} —10^{-7} normal, and in the form of paper is moderately serviceable, but generally inferior to azo-litmin. The color change is neither very distinct nor sharp.

Haematein. Test paper was made by saturating strips of good quality filter-paper in a freshly-prepared 0.1 per cent. alcoholic solution of the purest obtainable haematein, and allowing to dry without heat. The paper had to be kept in the yellow (acid) condition, as in the bluish purple (alkaline) state the color faded rapidly. The paper was rendered blue immediately before use by immersion in a *very* dilute aqueous ammonia solution, washing, and removing superfluous moisture by pressing between filter-papers, and then used in the moist condition. The end point of the titration is seen much more accurately if the paper is moist, as the mere moistening of haematein paper produces a slight change of color. It was also found that

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haematein paper, even in the acid condition, did not keep satisfactorily for more than one week. The end point of the titration was supposed to be reached when no yellow color was produced in the indicator paper immediately on spotting with the liquid under titration, since further color-changes almost immediately take place. The greatest difficulty is the extremely gradual nature of the color-change, the yellow color almost imperceptibly gives place to a yellowish pink very difficult to distinguish from it. The following particulars are taken from a paper by Salm, "Studie über Indikatoren" (*Zeit. für Physik. Chemie*, Band LVII., 1907, page 471) to which we are indebted for much of our information on this subject, and represent the color-changes of haematein from a hydrion concentration of twice normal to one of 10^{-15} normal hydrion concentration.

Hydrion concentration		Color
2	normal	raspberry red.
1	"	pink.
10^{-1}	"	green gray.
10^{-2}	"	greenish yellow slowly going gray.
10^{-3}	"	
10^{-4}	"	green yellow.
10^{-5}	"	
10^{-6}	"	brown with a trace of red.
10^{-7}	"	bright lilac.
10^{-8}	"	violet.
10^{-9}	"	red violet.
10^{-10}	"	red violet, turning brown.
10^{-11}	"	
11^{-12}	"	dark red violet.
10^{-13}	"	dark red, later slowly brown.
10^{-14}	"	dark red, later brown, then yellowish green.
10^{-15}	"	blue violet.

Salm remarks that most of the colors are not permanent. The present authors do not claim, of course, that all these variations in color could be observed without the use of a colorimeter, but they are sufficiently obvious in the normal course of experiments to explain certain peculiar color effects and to render haematein a very difficult indicator.

Acetic, lactic, gallic and benzoic acids and all strong inorganic acids are moderately well estimated by the use of haematein paper, while boric acid only produces a slight reddening. Cer-

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tain phenols in strong solution turn haematein paper reddish brown, but the color produced by such strengths of these bodies might be found in the liquors is very slight, and is readily distinguishable from the yellow color produced by bona-fide acids. The purest gallotannic acid which could be prepared was distinctly acid to haematein.

Azo-litmin paper was purchased. Changes color at a hydrion concentration of 10^{-8} normal. The color change is somewhat slow, and there are four distinct shades in it, viz.: a pink violet, violet, bluish violet and blue. The indicator did not prove very serviceable, and the readings obtained with the filtered and undetannized solutions were not very concordant. As used in Koch's method the indicator is somewhat unsatisfactory, and on the whole it does not compare very favorably with some others.

Phenolphthalein changes color fairly sharply at a hydrion concentration of 10^{-9} normal and seems to estimate a few bodies not included in the haematein value. It was not very serviceable with liquors either in the solution or as paper. By diluting the liquor and spotting on a tile fairly concordant results could be obtained. Its most prominent defect for our special purpose was the very decided alkalinity required to produce the color-change, which led to hydrolysis and oxidation of the tanning matters.

Alizarin only changes color when the hydrion concentration is below 10^{-11} normal, *i.e.,* in decidedly alkaline solution, and consequently is unsuitable for tan liquors for the same reason as phenolphthalein.

Fluorescein is an indicator which does not depend on an ordinary color-change, but on the appearance of green fluorescence, beginning at a hydrion concentration of N 10^{-5} and increasing to about N. 10^{-7}. It is used as an internal indicator in the solution, and is applicable even with dark-colored liquids. It is therefore an excellent indicator for estimating the total acidity of a tan liquor, and in *Collegium,* No. 419, we ventured to outline a method using the maximum fluorescence as end point. For six months, working with one sample of fluorescein, we obtained excellent results, but recently we have found that the personal equation involved by this method is much higher than we had previously reason to suppose. We have found that the stand-

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ard fluorescence obtained by adding excess of alkali to 10 cc. of tan liquor containing five drops of 2 per cent. alcoholic fluorescein solution was not always definite. We tried to overcome this difficulty by using the fluorescence produced by a solution of definite hydrion concentration, viz.: 10^{-7}, as standard, and hoped in that way to obtain perfectly definite results, but ultimately found that different samples of fluorescein gave slightly different fluorescence, and the amount of indicator solution added had a great effect on the result.

It has been found, not only by ourselves, but by colleagues in other parts of England, that the fluorescein method as outlined by us in the *Collegium* is capable of giving good results in the hands of one observer, but as we have previously stated, this is common to many methods. We are very reluctant to abandon fluorescein, as with its use a direct titration of the unfiltered liquor may be made with great accuracy, the real difficulty being to obtain a definite standard of color capable of being reproduced by different observers; and we shall be glad if leather chemists will assist us in making experiments in this direction as it is quite evident that this indicator is well worthy of our attention. We now propose to experiment with the following indicators kindly provided by the University Tinctorial Chemistry Department:—aesculin, methyl red, 1 : 4 amido naphthol benzaldehyde *o*-sulphonic acid, and an unknown fluorescing substance.

A considerable series of experiments was carried out to test the fluorescein method, and in most cases the concordance was very similar to that with haematein; close for any single practiced observer; less good for a variety of observers fixing their own standards, but a few observers seemed regularly to obtain results constant in themselves but differing from the majority. Congo red, methyl orange and haematein papers were also carefully tested by titration under petrol ether with different liquors and each gave results not differing among themselves at the most by more than about 0.2 cc. and usually much closer.

The following table shows the results obtained on a series of liquors containing the material of an ordinary mixed tannage taking that found by haematein which closely indicates the true point of neutrality as 100. Of course the actual relation only

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holds good for the individual liquors as it is dependent on the proportion of different acids present.

Indicator. Approx. Hion concentration	1	2	3	4	5	6	7	8
Azolitmin	106	100	104	104	109	..	..	..
Haematein	100	100	100	100	100	100	100	100
Fluorescein	88	89	93	87	62	..	..	..
Rosolic acid	88	93	93	92	66	..	..	..
Lime-water	82	96	93	..	69	49	65	63
Congo red	82	71	74	75	44	32	33	37

The last three liquors contained oakwood extract and oak bark only.

The figures of course represent the percentages of the total acid of the acids reaching the strengths or hydrion concentrations assigned to the various indicators. Acids which are not indicated by congo red have little or no plumping effect though they will still dissolve lime.

Below are given a few comparative results on four liquors from a light leather yard which were tested for acidity by the lime-water, haematein and congo red methods. The haematein and congo red were used as outside indicators with the separating funnel method before described. The big difference between the two latter indicators in all the readings was very puzzling, and can only be accounted for by the assumption that the liquors contained very few of the stronger acids.

Liquor No. I. Oakwood Extract and Oak Bark.

Acidity by
Lime-water = 25 cc. of liquor require 8.0 cc. N/10 alkali.
Haematein = " " " 16.0, 16.05, 16.05 cc. N/10 alkali.
Congo red = " " " 5.9, 5.8, 5.9, " " "

Liquor No. II. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 9.8 cc. N/10 alkali.
Haematein = " " " 15.25, 15.15, 15.10 cc. N/10 alkali.
Congo red = " " " 5.0, 5.0, 4.95 " " "

Liquor No. III. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 10.4 cc. N/10 alkali.
Haematein = " " " 16.5, 16.4, 16.5 cc. N/10 alkali.
Congo red = " " " 6.0, 6.1, 6.0, " " "

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Liquor No. IV. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 10.2 cc. N/10 alkali
Haematein = " " " 16.4, 16.3, 16.25 cc. N/10 alkali.
Congo red = " " " 5.9. 5.9, 6.9 " " "

Handler liquor, Valonia, Myrobs, Oakbark, and Chestnut 22° Bkr.

Acidity by
Lime-water = 25 cc. of liquor require 9.2 cc. N/10 alkali.
Haematein = " " " 14.4, 14.45, 14.5 cc. N/10 alkali.
Congo red = " " " 10.8, 10.7, 10.6, 10.6 " "

The above figures, which appear somewhat inexplicable, are given to show that the use of a number of indicators in the titration of a tan-liquor acidity seems to throw some light on its acidic composition and certainly conveys more information to the tanner. In these cases the haematein result might stand for the total acid value, that of the congo red for the total plumping value, and the lime-water for the lime dissolving power.

A number of interesting phenols and aromatic acids, which if they do not occur in the liquors at least form the basis of many tannins, were examined. We trust to publish more fully on this point at a later date. but it may be sufficient for the present to give the following results. We found that gallic acid was ionized to a much greater extent than protocatechuic acid in equivalent solution, *i.e.*, that gallic acid is the "stronger" acid and there can be little doubt that it possesses a slight plumping power. Both acids turn congo red paper blue.

Of the phenols pyrogallol and resorcinol are both acid to haematein, the former considerably and the latter slightly so. Neither produced any color-change in congo-red. Phlorogucinol did not affect either congo red or haematein.

It may be added that all these tests were performed on the purest obtainable products.

Discussion (at Leeds).

Mr. F. W. Richardson said that many of the suggestions in the paper might be very useful in general laboratory work, such as the determination of organic acids, where the question of dilution and the reagents used were very important. No two

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analysts, for instance, used phenolphthalein in the same way, and where very accurate results were required work with it was questionable. His experience with dilution methods was not very fortunate. The proposal to use the inversion of sugar as a criterion, reminded him that curious results were sometimes obtained when complex organic bodies were also present.

MR. A. G. PERKIN said that as yet there was no evidence of the presence of a carboxyl group in the natural catechol-tannins. It was possible that catechol-tannins might exist in nature, which were similar to the artificial product Schiff obtained by the condensation of two molecules of protocatechuic acid, and if so would be expected to possess an acid nature. On the other hand, it was hardly likely that such a compound would give the phlobophane reaction, so characteristic of the well-known catechol-tannins. In his opinion this property was not necessarily due to the presence of a catechol nucleus, but rather arose from the peculiar structure of the compound as in the case of catechin and cyanomaclurin, and this was evidently of a more complex nature than that possessed by gallotannin. According to numerous workers catechin is the parent substance of catechutannic acid and can be very easily converted into this compound, which seems to be a typical catechol-tannin. Such being the case, it was not easy to understand, in the light of (Kostanecki's) formula for catechin, how catechutannic acid could possess a carboxyl group.

DR. L. L. LLOYD said that if solutions contained any neutral salts there was the possibility of the production of mineral acids. Thus a mixture of wool and formic acid at a temperature above 50° tended to produce mineral acid which might hydrolyze tannin. Possibly leather might have a similar action.

DR. H. INGLE said that he always doubted the results obtained on titrating organic substances containing double linkages with alkali unless the atmosphere was absolutely excluded. Thus if saponification values of resins were done in open air there was a tendency to get an inaccurate result. Petroleum spirit did not altogether overcome the difficulty of the presence of atmospheric oxygen since by the law of partial pressures a little oxygen must be present. In the titration of highly colored liquids he had found certain sulphonated phenylrosaniline compounds very use-

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ful. Fluorescein was better, since the color impression in this case depended on reflected instead of transmitted light, and was therefore more or less independent of the color of the solution.

PROF. H. R. PROCTER said that the film of petroleum spirit on the surface of the liquid excluded air almost completely, and tannin substances were not very absorbent of oxygen in the acid condition. Difficulties in the use of fluorescein as an indicator were in obtaining a standard color for comparison. He believed that by the use of one or two acid salts, such as sodium hydrogen phosphate, along with Bismarck Brown, the color with fluorescein would be a good imitation of that of the tannin liquors. He suggested the use of flattened capillary tubes. These gave a fairly wide surface. One of the tubes should be used for the standard liquid, and the other should be a pipette with a bulb very much like a penfiller which could be dipped into the liquid. The drop removed could be returned after examination. He pointed out the difference between the strength of an acid, *i.e.*, its sourness, and its concentration. Sörensen had recently investigated this with regard to enzymes, by the use of indicators, but checking his results by the determination of the hydrion concentration electrolytically. Although he had rejected this method in practice on account of its difficulties, he intended to check indicators by actual electrical measurements, which were now comparatively easy by the employment of Dr. Sand's apparatus as used by Wood and Law. Indicators on paper often gave quite a different effect from that in solution. On the paper they were probably in colloidal combination, and therefore less likely to be affected by colloidal proteid.

MR. A. SEYMOUR-JONES said that whereas the lime-water method only estimated those acids which had soluble calcium salts, the fluorescein method estimated the potential and actual hydrogen ions. Fluorescein gave higher results than lime in the proportion of about 1.1 to 1.0. Petroleum spirit was sufficient for practical purposes. Sörensen had found that Congo Red was colloidal in character, whilst fluorescein was crystalloidal, as it belonged to the eosin group.

DISCUSSION (AT NOTTINGHAM).

MR. D. J. LAW said that in dealing with the acidity of tan

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liquors they were concerned with hydrogen ion concentration. The original hydrion concentration of the liquid future investigations would probably show to be related to its swelling power; on the other hand, there was the amount of alkali which had to be added until the liquid assumed approximately the hydrion concentration of pure water. This would be a measure of the capacity which the liquor would show for dissolving lime. The fact that methods for the determination of hydrion concentrations, involving the use of indicators, would always suffer from a certain lack of flexibility, more especially when dark liquids, such as tan liquors were to be investigated, would militate against their application when such problems as the relation of hydrion concentration to plumping effects were to be investigated. These considerations led Mr. J. T. Wood to suggest to Dr. Sand and himself that they should investigate the applicability of the electrometric method to the examination of tan liquors. The electrometric method, which was based on the determination of the difference of potential between the liquid under examination and a plate of platinized platinum saturated with hydrogen, was formerly more or less impracticable owing to complication of apparatus. Recently, however, the apparatus for such purposes had been so much improved by Dr. Sand for the purpose of the electro-analytical separation of metals (Trans. Faraday Soc., 1909, 5, 159) that its application was now an exceedingly simple matter. The results obtained so far, showed that for the titration of acids, such as acetic and lactic acid, added to given quantities of tan liquors, the electrometric method was easy of application and gave very satisfactory results. He hoped that the investigation referred to would shortly be completed when it would be laid before the Society.

Dr. J. Gordon Parker said in the past it had been assumed that lactic, formic, and similar acids were the panacea for all troubles, but until the effects of those acids had been thoroughly investigated by some method resting upon a scientific basis it was unwise to make such assumptions. He admired the simplicity of the electrometric process and hoped that the price of the apparatus would not be prohibitive.

Prof. H. R. Procter remarked that it was of the greatest importance to tanners to know not only the total quantity of

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acid present in a liquor, but its "strength" under the actual working conditions, since upon this its effect on the tanning process mainly depended. The "strength" differed greatly in different acids, and was proportional to the concentration of free ionized hydrogen atoms actually present in the liquor, which was measured directly and with great accuracy by the electrical method, and he congratulated Messrs. Sand and Law on having shown that the method was convenient and practical in the laboratory, since Mr. Seymour-Jones and himself had been deterred from attempting to use it in practice from its apparent difficulty with the ordinary apparatus, and had tried to solve the same question by the use of colored indicators in a less perfect but much more simple way.

MR. J. T. WOOD said he had the privilege earlier in the year of reading and judging Mr. Seymour-Jones' thesis for his B.Sc. degree, on "the acidity of tan liquors," and this caused him to give attention to the subject and read Salm's paper as well as to refer to the literature of the electrometric method by Böttger and others. Had it not been for Dr. Sand's loan of his potentiometer and his help in discussing the problems presented to the tanner, probably nothing would have come of it. He considered that it was the simplicity of Dr. Sand's arrangement which rendered the electrometric method practicable. He was sure it would give the tanner much useful information as to changes taking place in the liquors.

WATER OF CRYSTALLIZATION OF MAGNESIUM, ALUMINUM AND SODIUM SULPHATES WHEN PRESENT IN LEATHER.[1]

By Dr. J. Gordon Parker and M. Paul.

Nowadays sole leathers are frequently treated with various salts, including magnesium sulphate, sodium sulphate, and aluminum sulphate. These salts are used because of their cheapness; they are non-hygroscopic and contain a large proportion of water. When their amount does not exceed 6 or 7 per cent. of the weight of the leather, no crystallization takes place on the grain, and it is quite impossible by simple examination to see if the goods are adulterated. Moreover, in the

[1] *Journal of the Society of Chemical Industry*, Nov. 30, 1910.

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analyses, the percentage of ash is very low, due to the fact that dissociation takes place during the burning. Epsom salt especially is completely dissociated into magnesia, in such a way that one part of magnesia corresponds to 6.16 of $MgSO_4,7H_2O$.

These sulphates are determined in the ash, magnesium sulphate as phosphate,[1] aluminum sulphate as alumina, and sodium sulphate by estimation of sulphuric acid. The percentages which are obtained from the ash are calculated as hydrated salts. Generally, magnesium sulphate is reckoned with seven mols. of water, because it crystallizes in the air in this state.

Chemists do not agree concerning sodium and aluminum sulphates. This uncertainty sometimes causes big differences in proportion to the high percentage of water with which the salts may crystallize. For instance, the proportions of hydrated salt corresponding to one part of anhydrous salt are, according to the number of molecules of water of crystallization, as follows:—

Magnesium sulphate.—One part of anhydrous salt corresponds to 2.04 parts of $MgSO_4,7H_2O$, 1.74 parts of $MgSO_4,5H_2O$, and to 1.11 parts of $MgSO_4,H_2O$.

Sodium sulphate.—One part of anhydrous salt corresponds to 2.26 parts of $Na_2SO_4,10H_2O$, 1.63 parts of $Na_2SO_4,5H_2O$, and to 1.35 parts of $Na_2SO_4,3H_2O$.

Aluminum sulphate.—One part of anhydrous salt corresponds to 1.95 parts of $Al_2(SO_4)_3,18H_2O$, 1.63 parts of $Al_2(SO_4)_3$, $12H_2O$, and to 1.31 parts of $Al_2(SO_4)_3,6H_2O$.

The chemist knows that the method of calculation is somewhat optional, therefore this does not matter, but for the practical tanner who examines the analyses and sees only the percentages which are given to him,[2] it makes a great difference in his appreciation of the results.

This uncertainty is further increased, because the average moisture of ordinary sole leathers after some weeks of exposure to the air of a laboratory is between 16 and 18 per cent.;

[1] Levi & Manuel (Tanners' and Chemists' Handbook, p. 32), say that magnesium sulphate is found as the anhydrous salt in the ash. But when the burning to ash is done in a muffle furnace, magnesia is always found.

[2] The percentage of magnesium sulphate with 7 molecules of water calculated from the ash is always too great, because the magnesia from the water and from the lime used in the tanyard are counted in the same way.

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in determining the moisture of leathers containing 3 to 4 per cent. of sulphates (calculated as anhydrous salts by heating in the air oven at 100°—105° C. for three hours) we have frequently been surprised at not finding the corresponding increase of the amount of water coming from the water of crystallization, that is to say, about 3 or 4 per cent. This might be due to the difficulty of dehydrating the salt, but by heating in a vacuum for a long time till constant weight, we have only recovered this difference for magnesium and aluminum sulphates whereas with sodium sulphate the moisture was not very much increased.

We have therefore investigated the possibility of determining and verifying the amount of water of crystallization for the three above-mentioned salts in leather. For the other non-hygroscopic heavy salts, such as barium chloride, the ratio of water to salt is very low, and therefore the question is not an important one.

Curried leathers and leathers treated with various percentages of glucose have been tried, but we unfortunately got discordant results; with fatty leathers because the oxidation of the greases and oils is too variable, and with the leathers treated with glucose because very small variations in the moisture of the air produce great differences in weight, due to the hygroscopic nature of the glucose.

Therefore we give only the method and the results for sole leathers.

The microscopic examination does not reveal very much because these salts produce some non-crystalline precipitates with the soluble matters from the leather.

The principle of the process was as follows:—We took 12 pieces of leather, 4 in. square, from the same belly portion of the hide, before rolling, to get two sufficiently homogeneous series of six pieces each; after six days the moisture of each series was determined under the same conditions, taking one piece of 1 in. by 4 in. from each sample. For the two portions the difference in moisture was about 0.02 per cent.

The remaining two portions were left together in the air and weighed every day. The daily variations were the same, and for one month the greatest difference was 0.04 per cent. (average 0.009 per cent.).

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This point has been verified three times; once in operating as above, and twice with samples moistened with 25 per cent. of water.

Now, if one of the series is impregnated with a solution containing a known weight of anhydrous salt and the other one moistened with the same volume of pure water, and the two series allowed to dry in the air under the same conditions it will be possible to find out the amount of water which has been fixed by the salt. As the two portions are similar, the comparison between the weights of the two samples taken from time to time will show the relative increase of weight produced by the salt; the weight of anhydrous salt being known, the water from this salt and therefore the number of molecules of fixed water can be calculated.

This suggestion may be criticised from a theoretical point of view, but it answers sufficiently for practical purposes, because the interesting point is to see the relative increase in weight produced by a certain amount of salt.

We have made several experiments with each salt, using various proportions of anhydrous salts on the weight of the leather, varying the conditions of drying with various leathers containing different amounts of water soluble matters.

Sampling.—To allow of an easy impregnation we took porous ox hide bellies; after ordinary scouring and setting out, mineral oil was used for oiling instead of cod oil to produce a more porous grain. The drying was done at the ordinary temperature for three weeks, the experiments being carried out with samples of 3 in. square, six pieces for each group; all the pieces put together for eight days to arrive at an average moisture-content, and the weights taken every day to see the concordance of the variations.

The weights of the various groups were about 100 grms.

Impregnation with solutions of sulphates.—The salts used were pure recrystallized products. Solutions were made containing 16 per cent. of anhydrous salt at 20° C. The strength was determined by estimation of sulphuric acid for each salt, and estimation of magnesium as phosphate, and aluminum as alumina.

With these three standard solutions, three new series of solutions were made containing in 25 cc. of liquid 4 grms., 2 grms.

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and 1 grm. respectively of anhydrous salt in such a way that by using 25 cc. of the solution for 100 grms. of leather, the percentages of salts were respectively 4, 2 and 1 per cent. as anhydrous salt on the weight of the leather. With more than 4 per cent. the salt crystallizes on the outside. Each group of six pieces was impregnated with the 25 cc. of the corresponding solution. When the liquid is carefully run from a burette drop by drop on the grain and on the flesh side, it is quite possible to put 25 per cent. of liquid in a porous leather without any loss. Immediately after impregnation the leather was weighed to verify that no loss had occurred.

The groups with water were moistened with 25 cc. of pure water. The drying of the various groups was done exactly in the same way. The first at ordinary temperature of the laboratory (15°—18° C.), the second in the drying room at 22°—24° C., and the third at 28°—30° C. The second and the third groups were removed from the drying room as soon as the drying was normal to prevent the alteration which accompanies a more complete drying. All the samples put together were weighed three times a week for two months.

The variations of weight were in concordance six days after the impregnation for the drying at ordinary temperature, and after ten days for the other groups. Each group compared with the corresponding one treated with water gave the relative increase of weight produced by the amount of anhydrous salt, therefore the fixed quantity of water, and the number of molecules of fixed water could be calculated.

The numbers in the following table give the average of these determinations which were in concordance at each weighing.

On examination of the table we see that magnesium sulphate has taken about seven mols. of water for the leathers which are dried at ordinary temperature. This quantity decreases to five mols. for leathers dried at high temperatures. For aluminum and sodium sulphates, the difference is smaller, depending on the temperature of drying, the amounts being 10—12 mols. of water for aluminum sulphate and three for sodium sulphate.

The results also show that the percentage of soluble matter varying between 5 and 20 per cent. of the leather does not affect the quantity of water fixed by the salt.

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MOLECULES OF WATER FIXED BY

Percentage of anhydrous salt	Magnesium sulphate — Drying at 15°-18° C.	22°-24° C.	28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.1	5.4	3.1*
Leathers with 10 per cent. of soluble matter	7.1	6.0	5.2
Leathers with 5 per cent. of soluble matter	6.4	5.7	4.8
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.7	6.1	5.4
Leathers with 10 per cent. of soluble matter	6.5	5.3	3.3*
Leathers with 5 per cent. of soluble matter	6.8	5.0	5.1
One per cent. of the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.9	6.0	5.2
Leathers with 10 per cent. of soluble matter	7.2	6.2	4.9
Leathers with 5 per cent. of soluble matter	7.0	5.1	5.2

Percentage of anhydrous salt	Sodium sulphate — Drying at 15°-18° C.	22°-24° C.	28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	2.3	2.6	2.9
Leathers with 10 per cent. of soluble matter	2.9	2.8	2.2
Leathers with 5 per cent. of soluble matter	2.6	2.7	3.2
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	2.7	2.2	2.5
Leathers with 10 per cent. of soluble matter	2.4	2.9	2.7
Leathers with 5 per cent. of soluble matter	3.0	2.4	2.3
One per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	3.1	2.4	2.2
Leathers with 10 per cent. of soluble matter	2.7	2.7	2.8
Leathers with 5 per cent. of soluble matter	3.2	2.6	3.1

Percentage of anhydrous salt	Aluminum sulphate — Drying at 15°-18° C.	22°-24° C.	28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	11.2	9.9	9.6
Leathers with 10 per cent. of soluble matter	11.8	10.2	10.4
Leathers with 5 per cent. of soluble matter	11.4	9.8	10.8
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	11.5	10.1	10.0
Leathers with 10 per cent. of soluble matter	12.2	9.7	10.6
Leathers with 5 per cent. of soluble matter	10.1	12.3	11.3
One per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	12.8	10.9	10.7
Leathers with 10 per cent. of soluble matter	10.7	11.1	11.2
Leathers with 5 per cent. of soluble matter	11.0	11.2	9.8

The samples marked * show crystallization outside.

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In addition we have made some determinations with 100 grms. of small pieces of leather about 1 in. square, put in basins to facilitate the impregnation with the solutions, but the results were not satisfactory, because crystallization takes place on the surface of the samples and on the bottom of the basins; the number of molecules of water was always smaller than the number given in the above table.

Finally, we have made a determination with larger pieces of leather, with three groups of samples (500 grms. each); the first group with 3.5 per cent. of anhydrous magnesium sulphate on the weight of leather, the second with 3.5 per cent. of anhydrous sodium sulphate, and the third with the same volume of water, doing the drying at ordinary temperature. The results were for magnesium sulphate, 6.8 mols. of water, and for sodium sulphate 3.1 mols.

THE SEYMOUR-JONES ANTHRAX STERILIZATION METHOD.[1]

By Alfred Seymour-Jones.

For many years the terrible scourge of anthrax has exacted an annual toll of human and animal life from this and other countries, and the disease was rendered all the more awful in that until recently it was, except in the earliest stages, incurable. Now, however, thanks to the work of Drs. Fortineau and Sclavo, it seems apparent that human beings may, to a certain extent, be saved, even when in the actual grip of this deadly malady. One very important step in the extermination of anthrax in European countries and America is the disinfection of the anthrax-infected materials which are imported into these countries without inpairing their usefulness for the various manufacturing processes which they subsequently undergo. This part of the problem the present writer claims to have solved and, as will be seen, his claim is supported by a mass of experimental work, not only by himself, but also by leading experts of the country. The process to be subsequently described will effectually disinfect, without injury, dry and wet hides and skins, wool, mohair, horsehair, and similar materials which are carriers of disease.

[1] *Leather Trades Review.*

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The difficulty in solving the problem of anthrax sterilization has rested hitherto in discovering a method of sterilizing the anthrax spore when embedded in a gelatinous, aluminous or other colloid body, without injury to the material or fabric to be disinfected. The materials which act as carriers of anthrax are:—Hides and skins (especially when dry), wool, horsehair, mohair, rags, etc.

Sufficient evidence has been collected by the British Board of Agriculture and the British Home Office to warrant the supposition that animal foodstuffs, when imported, receive contagion from association with the foregoing materials, previous to importation. Assuming that this suspicion is justified, it follows that much, and probably nearly all the agricultural risks, can be eliminated, if the infected material is not placed in the neighborhood of such foodstuffs prior to shipment at foreign ports, by a thorough treatment of the infected material by means of some efficient sterilizing process at the port of shipment.

Any process which sterilizes hides and skins will naturally be applicable to their products, hair and wool, and consequently the adoption of a satisfactory method for the former should solve the difficulties in the latter and all other similar cases. At the same time the method must not interfere with any subsequent operation through which the disinfected material has to pass.

In all tropical and semi-tropical countries such as South America, India, China and Africa, hides and skins are dried either in the sun or in a shaded air current, or are plastered over with an earth salt while drying. The restoration of all such hides and skins to the green, raw, or wet state has always been a source of great difficulty and loss to the tanner, whose troubles were directly proportional to the method of curing and drying.

The method devised by the present writer overcomes in a quick and satisfactory manner the difficulty of sterilizing and restoring dry hides and skins to their former condition, and it is proposed that the whole operation should be carried out at the port of shipment before embarkation. To give full effect to the provisions of the method and to ensure that no industry is placed at a disadvantage, it would be advisable, if not necessary, that the leading Powers or Governments should agree upon a common course of action coming into operation after a given date.

The process proposed depends on the fact that an acid solu-

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tion is very readily absorbed by colloidal albuminoid substances, *e. g.*, blood, gelatine, or hide, the absorption being accompanied by a peculiar swelling of the whole treated material, due to a simple absorption of considerable quantities of water according to the osmotic laws. This swelling is known to tanners as "plumping," and has been specially studied with relation to gelatine by Professor H. R. Procter.

The usual place of secretion of anthrax spores is on the surface of and immediate inside of a colloidal albuminous mass, such as a blood clot, and the outer "skin" of the spore consists of similar albuminoid matter. The difficulty up to the present has been to obtain a disinfecting solution which would penetrate firstly the dried blood clot, and secondly the hard "skin" (cell wall) of the spore. The treatment with acid solution provides a way out of this difficulty, for it causes the clot and the spore to swell, absorb water, and become very soft and tender. The acid itself has a deleterious effect on the spores, but sterilization by it alone is not sufficient. The process provides for this by treating swollen and tender material with a very dilute solution of a most powerful bactericide, but this will be dealt with later.

Many experiments have been carried out with a view to finding which of the many acids at our disposal was the most suitable for the above-mentioned swelling.

The author's experiments have shown that the acids least likely to interfere with the useful character of the infected material are the organic acids. Of these formic acid is to be preferred owing to its high ionization constant, which makes it a very strong acid, and its low molecular weight, both of which factors contribute towards rendering it the most efficient and, in the long run, the cheapest organic acid to use. It may be completely removed by washing, and is a disinfectant for all classes of fungoid growths, for so long as it is present no moulds, etc., will appear.

Its effect upon anthrax spores, when used cold, is interesting, although at present unexplainable. Animals inoculated with anthrax spores in dry blood clots, which have previously been subjected to a 24-hour treatment in a cold 5 per cent. solution of formic acid, survive from five to nine days before death ensues. Complete sterilization is not effected with formic acid solution

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alone, but if the blood clots have been maintained at 90—95° F. for 24 hours in a 5 per cent. formic acid solution, then the subsequently inoculated animals survive the operation.

It would not be practicable to maintain any such temperature without a special and expensive plant to obtain it and keep it constant; therefore the employment of a powerful disinfectant is necessary when the operation has to be carried out with cold solutions. All the coal tar and similar disinfectants are impracticable for one of the following reasons:—

(*a*) They sometimes produce a tanning or tawing effect on the hide.

(*b*) They fail to penetrate the infected material.

(*c*) They adhere very strongly to the hair, wool or hide, and often communicate a strong irremovable aroma.

(*d*) In many cases they fail to sterilize.

Experiments were conducted with a considerable number of metallic salts as sterilizers and without going into the merits and demerits of each it may be stated that as a result of much work mercuric chloride ($HgCl_2$) was chosen as the most suitable bactericide. One of its great advantages lies in the fact that excellent results were obtained, even using extraordinarily dilute solutions of the salt, which were such as to render its use in the requisite concentration perfectly harmless to human beings.

A chart is given to show the rate of absorption of acid and mercuric chloride by hide; on the ordinate (perpendicular) is plotted the amount of the acid and chloride remaining in solution, while on the abscissa (horizontal) is plotted the time taken to absorb. As will be seen, the concentration of acid in the solution round the hide falls regularly and gradually, showing a perfectly uniform absorption of acid throughout the experiment. On examining the mercuric chloride curve, however, we find a different effect, for the concentration of the mercuric chloride actually increases during the first hour or so, thus showing that the water is more rapidly absorbed than the mercuric chloride contained in it. As soon as the hide becomes softened the chloride begins to penetrate, and afterwards the absorption is rapid and regular, until it becomes fairly constant, equilibrium being established. By this time the piece of dried hide is quite

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soft and completely disinfected, the whole process only taking 24 hours.

Professor H. R. Procter, M. Sc., and Professor Dr. Edmund Stiasny have reported that the treatment of hides and skins by this process has no harmful effect on the leather subsequently produced, and also state that this method of treatment is most efficacious in rapidly softening dried hides. The reports are appended.

Mr. Howard Priestman, the wool and textile expert of Bradford, has reported that the process has no deleterious effect on wool, and his report is given below.

The sterilization efficacy of the method has been the subject of investigation by Dr. Constant W. Ponder, who is carrying out researches into the question of anthrax on behalf of the Leathersellers' Company. His report will, it is hoped, in due course be published by the Worshipful Company of Leathersellers.

The method is also undergoing a searching examination by Dr. F. W. Eurich, bacteriological expert to the Bradford Anthrax Investigation Board, who are interested in the wool and mohair problem, and he will, in due course, report to his Board, who will doubtless publish the results.

Below are given the details of the method of disinfection, and if carried out abroad the procedure in the case of wool and mohair requires no modification. If, however, the sterilization takes place in countries where a higher temperature can be conveniently obtained, in the latter case such a temperature, not exceeding 130° F. for wool, or 212° F. for hair, is not only permissible, but considerably accelerates the process. It is, of course, obvious that no raised temperature can be employed in the case of hides and skins

REPORT OF EXPERIMENTS ON THE CURE OF HIDES WITH FORMIC ACID AND SALT MADE AT THE REQUEST OF A. SEYMOUR JONES, ESQ.

Half of a dried China hide was soaked in a ½ per cent. solution of formic acid (the formic acid used being 40 per cent., the dilution was 1:80). After 12 hours a very considerable soaking effect was noticeable; the soaking was continued for 48 hours, when the hide appeared sufficiently soft. Now, a saturated salt solution was prepared and the hide allowed to remain in this

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for another day or two, when the hide was dried. A piece of this dried hide was easily soaked back again in cold water, behaving as ordinary salted hide.

The other half of the dried China hide was treated in a similar way, the concentration of the formic acid solution being 5 per cent. This hide, after the acid and salt treatment was washed with water in the drum, then limed with a sulphide lime (10 days), unhaired, fleshed and scudded. In this state it looked very well and was sent to Penketh Tannery to be tanned for sole leather.

As far as experiments on so small a scale allow any judgment, it may be stated that the treatment of dry hides with a dilute formic acid solution and subsequently with saturated salt solution has a very good soaking effect, the hides, after being washed out from the salt, behaving in the limes like fresh salted hides would do.

Drying out after salting does not affect this behavior, as resoaking is very easily effected.

H. R. Procter.
Edmund Stiasny.

Leeds University
June 27, 1910.

The China half-hide was sent, after liming, unhairing and fleshing, to the Penketh Tanning Company to be tanned along with their ordinary goods. No intimation was conveyed to them of its previous treatment.

Mr. C. E. Parker writes as follows:—

"The side that we got through you from Leeds is now finished. It weighs 20 lbs., and the leather looks all right. We do not notice any difference between our own sides and this."

It will not escape observation, that the foregoing side was treated to an acid solution, five times stronger than recommended to be employed in the process.

Report on the absorption of $HgCl_2$ by hide substance.

The point to be examined was the rate of absorption. To this

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end 87.5 grams of dried hide were cut into small pieces about 1 inch square, and immersed in 1 liter of 0.5 per cent. formic acid + $\frac{1}{10,000}$ $HgCl_2$ solution.

The experiment was started at 11.05 A. M. and hide was not completely softened by 5.35 P. M. When examined at 9.05 A. M. next morning was quite soft:—

THE CONCENTRATION OF $HgCl_2$.

At 11.05 A. M	1	part in	10,000
At 11.35 A. M	1.1	parts in	"
At 12.05 P. M	0.97	"	"
At 12.35 P. M	0.92	"	"
At 1.05 P. M	0.88	"	"
At 2.05 P. M	0.82	"	"
At 2.35 P. M	0.70	"	"
At 3.05 P. M	0.56	"	"
At 3.35 P. M	0.37	"	"
At 4.05 P. M	0.35	"	"
At 4.35 P. M	0.34	"	"
At 5.05 P. M	0.32	"	"
At 5.35 P. M	0.31	"	"
At 9.05 A. M. next morning less than	0.10	"	"

In the earlier stages water is apparently more rapidly absorbed by the hide than $HgCl_2$. Consequently the concentration of the latter increases.

The result of the above experiment as regards the total quantities is as follows:—

Amount of $HgCl_2$ absorbed by the hide up to 9.05 A. M.

= 0.0935 grams.
= 93.5 per cent. of original amount of $HgCl_2$.
= 0.13 per cent. on the dry weight of the hide.

DUPLICATE EXPERIMENT.

97.5 grams of dry hide in one piece immersed in 1 liter of 0.5 per cent. formic acid solution and $\frac{1}{10,000}$ $HgCl_2$ solution. Experiment was started at 11.05 A. M. Hide not soft at 5.35 P. M., but quite soft at 9.05 A. M. next morning.

The course of absorption was as follows:—

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THE CONCENTRATION OF $HgCl_2$.

At 11.05 A. M	1	part in	10,000
At 11.35 A. M	1.08	parts in	"
At 12.05 P. M	0.97	"	"
At 12.35 P. M	0.95	"	"
At 1.05 P. M	0.94	"	"
At 2.05 P. M	0.93	"	"
At 2.35 P. M	0.93	"	"
At 3.05 P. M	0.93	"	"
At 3.35 P. M	0.92	"	"
At 4.05 P. M	0.92	"	"
At 4.35 P. M	0.91	"	"
At 5.05 P. M	0.80	"	"
At 5.35 P. M	0.72	"	"
At 9.05 A. M. next morning	0.47	"	"

The phenomena are the same as in Experiment 1, but the absorption is slower owing to the hide being in one piece.

Amount of $HgCl_2$ absorbed = 0.0695 grams.
Amount of $HgCl_2$ absorbed = 69.5 per cent. of original $HgCl_2$.
Amount of $HgCl_2$ absorbed = 0.073 per cent. on weight of dry hide.
Temperatures of solutions = 70 degs. F.

This work was carried out under my supervision.

HENRY R. PROCTER.

September 12, 1910.

REPORT AS TO THE SOLVENT ACTION OF A 5 PER CENT. SOLUTION OF FORMIC ACID ON HIDE SUBSTANCE.

Liquor taken in which a China hide had been soaked until soft. No dissolved hide substance was detectable in this liquor by the Kjehldal process.

July 5, 1910.

This work was carried out under my supervision.

HENRY R. PROCTER.

REPORT OF THE ABSORPTION OF MERCURIC CHLORIDE (CORROSIVE SUBLIMATE) BY DRIED HIDE IN ACID SOLUTION.

Four solutions were made up, each of which contained 1 part of mercuric chloride in 10,000 of water. In addition solutions A and B were both 0.5 per cent. solutions of formic acid and solutions C and D were 1.0 per cent. solutions of formic acid. Four pieces of dried China hide were cut as far as possible into uniform sizes and shapes, and one piece immersed in each of the

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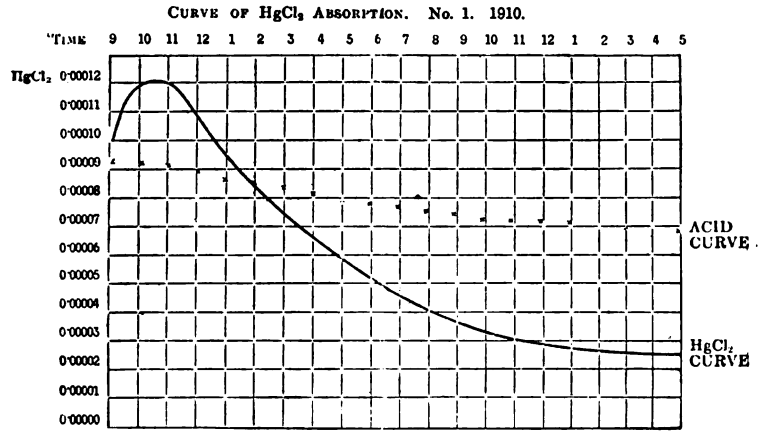
four solutions respectively, the volume of each solution being 1 liter. In these the pieces of hide remained for 24 hours, the acidity of the solutions and the concentrations of $HgCl_2$ being determined every hour. The results are given below.

N.B—The initial acidity of the liquors as described was only approximately produced by rough weighing. The initial concentration of $HgCl_2$, however, was most accurately obtained.



THE "SEYMOUR-JONES" ANTHRAX STERILIZATION PROCESS APPLIED TO HIDES IN DRY STATE.

A pit of suitable dimensions is required for the immersion of the hides.

Into the pit run sufficient cold water to cover the hides contained in the pit.

The volume of water must be a known amount.

To this volume of water add 1 per cent. of formic acid of 90 per cent. strength then after plunging to mix the acid and water, add 1 part mercuric chloride to every 5,000 parts of water. The mercuric chloride should be previously dissolved by heating in water. Finally plunge the whole pit well before adding the hides.

In this pit the hides are left for 24 hours, when it will be observed that their condition is somewhat similar to that of a

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Readings of $HgCl_2$ Experiment in Absorption

	No. 1 Weight of hide 110 grams		No. 2 Weight of hide 102 grams	
Time	Sol. 0.5% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration of $HgCl_2$	Sol. 0.5% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration $HgCl_2$
9.0	9.3	0.00010	9.3	0.00010
10.0	9.2	0.00012	9.2	0.00011
11.0	9.15	0.00012	9.0	0.00011
12.0	8.9	0.00010	8.9	0.00010
1.0	8.75	0.00009	8.7	0.00010
2.0	8.65	0.00008	8.6	0.00009
3.0	8.40	0.00008	8.4	0.00009
4.0	8.2	0.00007	8.35	0.00008
5.0	8.0	0.00006	8.30	0.00007
6.0	7.9	0.00005	8.15	0.00007
7.0	7.8	0.00004	8.05	0.00006
8.0	7.6	0.00004	8.05	0.00006
9.0	7.5	0.00004	8.0	0.00006
11.0	7.3	0.00003	7.75	0.00005
1.0	7.2	0.00003	7.70	0.00003
3.0	7.1	0.00003	7.6	0.00003
5.0	6.95	0.00002	7.5	0.00002

	No. 3 Weight of hide 111 grams		No. 4 Weight of hide 105 grams	
Time	Sol. 1% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration of $HgCl_2$	Sol. 1% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration $HgCl_2$
9.0	17.8	0.00010	18.6	0.00010
10.0	17.75	0.00012	18.3	0.00012
11.0	17.70	0.00011	18.15	0.00010
12.0	17.6	0.00010	17.6	0.00010
1.0	17.5	0.00009	16.8	0.00009
2.0	17.2	0.00009	15.95	0.00009
3.0	17.10	0.00008	15.7	0.00008
4.0	17.0	0.00007	15.55	0.00008
5.0	16.7	0.00006	15.4	0.00006
6.0	16.6	0.00006	15.25	0.00006
7.0	16.5	0.00005	15.0	0.00006
8.0	16.3	0.00005	14.75	0.00005
9.0	16.1	0.00005	14.6	0.00005
11.0	15.7	0.00004	14.45	0.00004
1.0	15.6	0.00003	14.25	0.00003
3.0	15.05	0.00003	14.0	0.00003
5.0	14.8	0.00002	13.8	0.00002

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raw hide, only firmer. This pit completes the act of sterilization. From the sterilization pit the hides should be drawn and allowed to drain in such a manner as will permit the liquor to flow back into the pit for further use.

After draining the hides are transferred to a pit containing a saturated solution of common salt and water. In this case it is advisable to have a good layer of undissolved salt lying on bottom of pit before immersing hides. In this pit the hides need not be left more than one hour, when they should be hauled up and placed on a drainer, in order that the salt liquor may return to the salt pit for further use. Or if it is found more convenient the hides may be opened out flesh up and hand salted, then placed in pile for a few days before baling. Or they may be again dried.

After draining, the sorting or classing, weighing and bundling may be proceeded with prior to export.

THE "SEYMOUR-JONES" ANTHRAX STERILIZATION PROCESS APPLIED TO GOAT AND SHEEP SKINS IN THE DRIED CONDITION.

A pit of suitable dimensions is required for the immersion of the skins.

Into this pit run sufficient water (cold) to cover the skins contained in pit.

The volume of water must be a known amount.

To this volume of water add one-quarter to one-third of 1 per cent. of formic acid of 90 per cent. strength, then after plunging to mix the acid and water, add 1 part of mercuric chloride to every 5,000 parts of water. The mercuric chloride should be previously dissolved by heating in water. Finally plunge the whole pit thoroughly before adding skins.

In this pit the skins are left for 24 hours, when it will be observed that their condition is somewhat similar to that of a raw skin, only firmer. This pit completes the act of sterilization. From the sterilization pit the skins should be drawn and allowed to drain in such a manner as will permit the liquor to flow back into the pit for future use. As skins usually have long hair or wool, this draining may be expedited by placing boards and heavy weights on the pile to exert a pressure.

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After draining the skins may be transferred to pit containing a saturated solution of common salt and water. In this case it is advisable to have a good layer of undissolved salt lying on the bottom of the pit before immersing skins. After lying in the salt solution one hour they can be hauled up and drained as in the case of the sterilization pit.

Or if it is found more convenient the skins may be opened out flesh up and the salt strewn on flesh side liberally, then allowed to remain in a pile for a day or so until salting is completed. Or they may be again dried.

They are now ready for classing, weighing, etc.

COST AND ECONOMY OF THE PROCESS.

The economical working of the Seymour-Jones process may be controlled by anyone with average intelligence. It is estimated that, buying formic acid at 5d. per lb., and mercuric chloride at 2s. 6d. per lb., the cost of the process will work out at about 3¾d. for a large hide and, of course, proportionately less for skins or wool.

As will be seen from the results of the work carried out at Leeds University, the amount of formic acid absorbed by the hide varies approximately from 20 to 25 per cent., leaving 80 to 75 per cent. still in the pit. Consequently, it is unnecessary to have a fresh bath for every lot of infected material, for if we start with a fresh solution, and after one lot of material 25 per cent. of our acid is taken up, on the second occasion the bath will only have to be strengthened to that extent, thus effecting a considerable saving.

The question of the analytical control of the mercuric chloride concentration is more complicated, and while the report and method of Professor Procter and Mr. Arnold Seymour-Jones is appended, I do not think it is at all necessary to follow it up in practice because as will be noted from the charts herewith, in the case of the hides and skins, nearly all the mercuric chloride is absorbed. It is therefore suggested that, unless there is suitable apparatus on the spot for carrying out the control as outlined in the analytical report, the pit be recharged each time with 1 part of mercuric chloride per 5,000 parts of water in the pit.

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A point of interest is that the Seymour-Jones process is very efficacious in preserving hide substance. As is unfortunately only too well known to the tanner, dried hides and skins in soaking back are apt to lose a relatively large percentage of their weight owing to solution of the decomposed skin matter. By effecting a thorough sterilization and cure of the hide or skin shortly after it comes off the animal's back, the Seymour-Jones process prevents putrefaction, and if the proposals embodied in this paper be properly carried out, it cannot be doubted that the loss due to this cause will be considerably diminished.

To increase the economy the following method specially worked out for the control of this process at the University of Leeds is given below.

THE ANALYTICAL EXAMINATION OF A 1.0 PER CENT. FORMIC ACID AND A 1 IN 10,000 MERCURIC CHLORIDE SOLUTION.

I. Estimation of the Acid.—This is accomplished in the usual way by titration of an aliquot part of the solution with decinormal sodium hydroxide in the presence of phenolphthalein. Each cubic centimeter of N/10 NaOH required corresponds to 0.0046 grms. of pure formic acid.

II. Estimation of the Mercuric Chloride ($HgCl_2$).—This estimation depends on the fact that mercuric chloride in such low concentrations as we are considering, in the presence of formic acid on treatment with sulphuretted hydrogen (H_2S) gas is converted into mercuric sulphide which remains in colored colloidal solution. We have determined by experiment that the depth of color of this solution is practically directly proportional to the concentration of the original mercuric chloride. The experimental details used in the present case were therefore, as follows:—

Ten cc. of the 1 in 10,000 mercuric chloride acid solution are pipetted into a test-tube and saturated with sulphuretted hydrogen gas. The colloidal mercuric sulphide solution so produced is poured into the dipping vessel of a Schmidt and Haensch dipping colorimeter, and the stage so adjusted that the solution under observation is exactly 10 millimeters thick. If the means are at hand this color can be most accurately matched with Lovibond's standard tinted glasses (red, yellow, and blue), and

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this forms a convenient permanent standard. As a rule, however, it is quite sufficient to use the color produced in a 1-centimeter cell by a solution of 1 in 10,000 $HgCl_2$ + 1.0 per cent. formic acid freshly precipitated with sulphuretted hydrogen gas.

The 1-centimeter cell of this standard color is placed on the matching platform, and into a clean, dry dipping vessel are pipetted 10 cc. of the acid $HgCl_2$ solution of unknown concentration previously saturated with H_2S. By manipulation of the dipping stage we then proceed to determine the depth of this solution which will match the standard color. This is accomplished by varying the depth of the liquid examined until a uniform field is obtained in the telescope. Let us suppose that the depth so found is x millimeters, then

$$\frac{\text{The concentration of standard}}{\text{The concentration of the unknown}} = \frac{10}{x}.$$

Knowing the concentration of the standard and the value of x, we can calculate the value of the unknown. We may thus determine the concentration of any formic acid mercuric chloride solution between 1 part in 10,000 and 1 part in 100,000 with very reasonable accuracy.

We have only used this method of estimation of mercuric chloride in the presence of formic acid, but experiments are now proceeding to determine if it is possible to perform it in the presence of other acids. We have found by extended tests that an observer being given a solution of mercuric chloride and formic acid, the concentration of which was unknown to him but known to others, can estimate very exactly the concentration of that solution by this method.

Although in our experiments the colorimeter used was a Schmidt and Haensch, a Dubosc or any other form of dipping colorimeter may be used instead.

(Signed) HENRY R. PROCTER.
ARNOLD SEYMOUR-JONES

Re INVESTIGATIONS FOR MR. A. SEYMOUR-JONES.

I have now completed all the laboratory investigations which are possible in regard to the effect of formic acid upon wool. Anything more complete would need the active co-operation

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of some spinner or comber who would be willing to experiment on a large scale.

Formic acid is now in common use in the trade, and is considered so much the best acid for certain dyeing purposes that its high price does not prevent its use.

To make sure of my ground I began by steeping fine clean Botany wool in 90 per cent. formic acid for 12 hours. This treatment made no alteration in the condition or prominence of the scales or serrations, or on the nature of the fiber when seen under a microscope giving 200 magnification.

I have steeped limed slipe in 90 per cent. formic acid for 12 hours without discovering any effect on the serrations of the fibers, although the "handle" of the wool was greatly improved by the removal of the lime and lime combination.

I have tried steeping both the above qualities in 20 per cent. solution and 5 per cent. solution of formic acid, transferring them to saturated salt solutions after four hours' or more immersion. None of these experiments have any effect on the scales or serrations of the fibers.

See micro-photographs herewith.

Magnification 226 times.

To discover whether either the acid or the salt had any effect on the strength or softness of the fiber I prepared 24 hanks, each composed of 40 wraps, 1½ yds. in circumference, 2/18 fine Botany yarn, and I append tables of breaking strains:—

SAMPLES.

	1 Four hours acid 20%. 45 min. salt	2 Four hours acid 5%. 45 min. salt	3 Forty-five minutes salt	4 Not treated
	..	62½	..	..
	..	63½	61½	62½
	62½	65	65	62½
	64½	64	63½	62½
	61½	61½	62½	61½
Total	187½	317½	252½	249
Aver.	62½	63½	63⅛	62¼

No. 1 was steeped four hours in 20 per cent. formic acid and 45 minutes in saturated solution of common salt.

No. 2 was steeped as directed—four hours in 5 per cent. formic acid and 45 minutes in saturated solution of common salt.

No. 3 was steeped 45 minutes in saturated solution of common salt.

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No. 4 was not treated in any way.

All the hanks treated are apparently stronger than those not treated.

This slight variation of less than 2 per cent. is doubtless due to slight variation in the yarn itself. Such variations are always present, and it may be taken that the treatment does not affect either the strength or the handle of the yarn.

Yours,

March 18, 1910. HOWARD PRIESTMAN.

I have just completed another series of tests as to the effect of 5 per cent. formic acid and saturated salt solution at 40 to 50° C.

I can detect no alteration in the microscopic structure, and I doubt if steeping alone in the solutions would have any effect whatever.

In order to keep the temperature regular I had to move the yarns very frequently, and to this is doubtless due the irregularity of the tests, because it would disturb the arrangement of the threads composing the various hanks.

As things are there is only a reduction of 1½ per cent. in the average strength, and I do not think that this small reduction would have any appreciable effect on the class of wool which is usually associated with anthrax.

I am, yours truly,

April 14, 1910. HOWARD PRIESTMAN.

Report on four hanks, each containing 40 wraps or 80 threads, 2/18 fine Botany yarn, all steeped four hours in 5 per cent. formic acid at 105 to 108° F., and for half an hour in saturated solution of salt at the same temperature:—

1st hank	58½ lbs.
2d hank	56½ "
3d hank	65½ "
4th hank	64 "
	4)244½ "
Average strength	61⅛ "

This is a reduction of 1½ per cent. on the untreated yarn.

April 14, 1910. H. P.

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ABSTRACTS.

The Mouldiness of Leathers. From *"Les Laines et Cuirs"* through *"Le Cuir,"* 1910 (3), No. 23, pp. 649 and 651.—The first condition for avoiding the mouldiness of leather is to keep the walls, floor and pillars very clean, whether it is during the drying or in the store houses. The filthiness which often exists there is the principal cause of the growth of mould. In many tanneries mould comes from old rinsing vats These vats should never be more than three feet in depth so that they can be easily cleaned. Too long a use also causes a thick growth of mould in them.

To avoid mould in store-rooms the best method is to entirely empty them from time to time, and fumigate them with sulphur. If this cannot be done, the floor may be sprinkled with very dilute hydrofluoric acid. In this case great care must be exercised because this acid is very corrosive and its fumes easily attack the respiratory organs.

Certain persons recommend formaline for the same purpose, but it does not appear that this would be as efficacious. A 5/100 per cent. solution of sublimate is certainly better for destroying mould germs in posts and the rods of the dryers, etc.; but being rather unstable, the substance does not hinder the development of germs for long. A 2 per cent. solution of fluoride of sodium which can also be used on leather itself is very much better. One should always specify, in procuring this substance that the pure and entirely soluble salt is desired, for it is often adulterated with fluoride of silicon which does not possess the same antiseptic properties.

The mouldiness of leather may often come from casks containing the oil with which it is treated. This is prevented by heating the oil before using and allowing it to cool again. A little salicylic acid added to the oil also destroys mould germs.

The Treatment of Mouldy Leathers. From *"Laines et Cuirs"* through *"Le Cuir,"* 1910, (3), No. 22, pp. 610 and 611.—When a leather merchant perceives that some of his goods are mouldy, alarmed by this discovery, he generally makes the great mistake of wishing to get rid of the mould as quickly as possible by rubbing or brushing. But this mould is damp and sticky, so that by such an operation exactly the opposite result is obtained from that hoped for. Instead of disappearing, the mould is fixed still more strongly on the leather in being pressed on the surface with rags used for rubbing or with the brush, thus becoming thin and more visible than before. If mould is to be removed from leather, it is necessary first to take the leather from the place where it became mouldy and to dry it. This drying may be done in the open air if the weather permits or in a warm place in case of rain. The cause of mould is removed in this way and also the mould itself is made easily removable. In fact when mould is dried, a brush or small broom will take it off without leaving any very marked traces on the surface of the leather. For thick leather the operation may also be

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facilitated by spreading on the surface very dry bran, which the brush removes together with the mould. The bran cleans the pores of the leather and besides it leaves in the small holes in the surface, traces of the meal, which help greatly in giving a certain gloss to the leather which too deep a mould would have tarnished considerably. It is very important that the bran in question should be used perfectly dry, and that it should never be used more than once.

The leather from the surface of which mould has been taken is then vigorously rubbed with a suitable rag. If the leather is black it is again rubbed with a rag soaked in bone oil. For chestnut leather the oil is replaced by soapy blacking. This rubbing restores the shade of the leather and gives it the luster which it had lost. Very rarely a new application of dye is made.

It is unnecessary to mention that leather cleared of mould is very often exposed to the same conditions which caused the mould. People seem to believe that the mould proceeds from the leather alone, and that the first cleaning guarantees it against further accident of the kind. Mould germs always exist in places where leather is. Therefore most particular care should be taken with leather which has once been mouldy, and it should be separated as far as possible from that which might injure it anew. If possible this leather should be placed in a very dry place. When this is not possible, and if it must be stored in the same room, this should at least be aired and cleaned, and subjected to frequent airing whenever good weather permits. It is also well to coat the walls and floor of the room with an antiseptic and to repeat the operation from time to time.

Finally, preparations should not be used for restoring luster to cleaned leathers, which themselves contain mould germs, and which afford excellent nourishment for microbes. Preparations consisting of blood albumin, glue, etc., are of this kind. These substances favor the development of germs which attack the leather. They should therefore be used only with moderation and after sterilization.

Bookbinding Leather; its Nature, Decay and Prevention of Same. Dr. Loubier. *Zentralblatt f. Bibliothekwesen*, 1910, pp. 322-49.—This paper by the custodian of the library of the Kunstgewerbe Museum in Berlin is based upon the reports of the special committee on bookbinding leather of the London Society of Arts 1901-5 supplemented by his own experiences. Systematic inquiry has shown that early bindings are durable, but that there has been a falling off since 1830 and those made since 1860 have shown the least endurance. The "red decay," whereby the leather becomes burnt, red and brittle is the most striking; in the form prevalent since 1860 the leather actually rots to a powder. The decay is independent of the amount of use and is most marked in well lighted and heated rooms. Since the ancient leathers have withstood, exposed to the same conditions, the essential cause must lie in the manufacture of the leather itself.

The leathers used in bookbinding are: (1) Goat leather (morocco)

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for superior bindings, manufactured in Europe, Africa and the East; the foreign leathers are native tanned and dyed in Europe. This leather is used both with natural grain and grain pressed. (2) Calf leather, smooth, without grain, vegetable tanned, plain and dyed. (3) Sheep leather; in Germany, "bock" leather means the East Indian sheep; split leather is generally sheep. (4) Pig skin leather, natural color or dyed yellow brown. (5) Seal skin leather, with fine natural grain or coarse, artificial grain. (6) Cow skin leather, little used.

With regard to the nature of the tannage, it has been found that the pyrogallol tans, especially sumac and gall-nuts, have proved the best. Oak is not injurious, but the red color produced is unsuited for dyeing. The so-called Niger leather from Guinea is said to be tanned by the natives with a species of gall-nut. The catechol tannins, such as quebracho, have shown themselves injurious, containing acids which attack the leather. The East Indian or "Persian" morocco and sheep skins have proved the least durable of all bindings, showing red decay in a year.

In the dyeing of leather, formerly only vegetable dyes were used. Since 1870 the coal tar dyes have been employed; the frequent use of sulphuric acid to intensify the color has greatly shortened the life of much binding. Another source of this injurious ingredient in leather is its use as a pickle. As for the dyes themselves, experiment has shown that many coal tar dyes give just as durable, light fast hues as the vegetable colors; care need only be given to avoid strong acids and harmful mordants. Dr. Lamb examined 1,500 samples of leathers dyed with coal tar colors and found red, blue and black the most durable towards light. The author exposed red brown Niger leather to direct light for 6 weeks and found the color held very well.

With respect to currying, the leather is often too much degreased by the acids used in tanning and dyeing. In spite of the greasing given in currying, the bindings often become too dry in the heated libraries. An attempt has been made to remedy this by oiling the bindings with vaseline or degras.

Artificially grained calf and sheep leathers are unsuited for bindings, the durability being lowered by the hot pressing used in the manufacture. Split leather is also too weak. Sheep is the softest and loosest of all binding leathers, but is more durable than bookbinders generally admit; it should not be shaved too thin and must be tanned and dyed without acids. Pig skin is strong but suited only for heavy volumes and it easily soils. The new Russian leather has little endurance although it has been highly rated. A discussion follows of the details in the mechanical work of binding and its best practice. Lastly the author treats of the best conditions for preserving bindings; hot air, vapor from gas lights, direct sunlight are all injurious. A plea is made for official inspection of binding leather and the requirement of guarantees from the manufacturer.

W. J. K.

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Fundamental Rules of Practice, (continued). L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, 217-9, 369-71.—A further advantage of extraction in closed vessels is in the possibility of transferring the liquors by pressure instead of pumping, this method being cheaper, better and quicker. The pressure may be applied by direct steam or compressed air. Although it has been previously shown that extraction under pressure decomposes some tannin, this evil need not be feared on merely subjecting the *surface* of the liquor to steam pressure to drive over the liquor. This can be easily verified by thus driving over cold liquor and it will be found that this remains cool up to the last portions which finally consist of a little warm condensed water. The spent bark becomes a little warmed and on this account it is better to use compressed air which is cheaper. The disadvantage of pumping hot liquors as is necessary in open extractors is that the hot liquor evaporates in the rarefied chamber of the pump and the exhaustion must be further increased; if too hot it cannot be pumped at all, until cooled off. Further, the bark is not so fully freed of liquor by pumping but contains 6-10 per cent. more water than when pressure transmission is used. Also the surplus or dead liquor below the perforated bottom of the extractor is greater in open vats and therefore the degree of the following extraction is proportionally lessened. The author found that on entire removal of the residual liquor from an open vat, the bark was 0.2 per cent. better extracted. Another advantage of extraction in closed vessels is the production of a lighter colored liquor; although apparently dark, on dilution to the same strength as the vat liquors, it is lighter. The author concludes from his own extensive experience that for the same space, closed extractors perform twice as well as open leaches.

In computing the loss of tannin in spent bark from the analysis, it is erroneous to reckon as is often done, the direct percentage of tannin found as loss in the original material. If for instance a pine bark yields up 20 per cent. of its total weight on extraction, and the spent bark be found to contain 2.5 per cent. tannin, this correctly computes to only 2 per cent. loss as based on original substance. It is further incorrect to reckon the tannin left in the bark as lost on the theoretical ground that it is all available for tannage. The author has earlier pointed out in the Report of the Freiberg Tanning School for 1903-4 that in the weak solutions used in tannin analysis substances are present and are estimated as tannin which would separate in the strong liquors of the tannery and remain useless. To properly judge whether a bark is sufficiently extracted, the spent material is examined and regard paid to its nature and the behavior of the liquor. If the last decoction which at the most shows 0.5 B., on standing and cooling gives a copious sediment and if the liquor by further warming and extraction of the same bark cannot be further enriched, then the practical limit is reached. The tannin content of this spent bark may serve as a standard and regular examinations of spent bark will be of great use in plant control. For greater accuracy hydrometers graduated to

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1/100° B. are used with the last liquors. To ensure no loss, the tannin content of the spent bark may be let reach 0.3-0.5 per cent. less than found in the above experiment, if conditions permit. Eitner showed in 1907 (abstr. this JOURNAL, II, 370) that in the analyses of fresh pine bark substances are extracted and rated as tannin which in practical extraction remain insoluble and although higher temperatures yield more extract, the proportion of sediment on cooling increases. It is not correct therefore to compute all the tannin left in the bark as loss nor all that is extracted as gain. W. J. K.

A Sensitive Reaction of Glue. E. SCHMIDT. *Chemiker-Ztg.*, [34] 839. —If to an aqueous solution of glue the ordinary acidified ammonium molybdate (phosphoric acid reagent) be added, a white precipitate is formed. Neutral molybdate does not give the reaction, this first appearing on addition of a few drops of dilute nitric acid, this is the preferable method in using the reaction, which is very delicate and characteristic. The precipitate and supernatant liquid become pale bluish green after standing. The method is well suited to test the materials used in dressing leather; concentrated solutions of gum arabic, linseed, and white of egg were found to give only a slight cloudiness which is easily distinguished from the glue reaction with practice. The author hopes to employ the method for gravimetric determination and is experimenting in this direction. W. J. K.

PATENTS.

Apparatus for Evaporating Solutions. U. S. Patent No. 980,108. SAMUEL MORRIS LILLIE, Philadelphia, Pa.

An essential feature of the method consists in passing the gases of combustion from the fire through a vertical flue, down which the liquid to be evaporated is sprayed.

Vacuum Drying Apparatus. U. S. Patent No. 980,444. OLIVER S. SLEEPER, Buffalo, N. Y.

Cylinder Grinder for Leather-Shaving Machines. U. S. Patent No. 980,561. OSCAR REIRSON, Peabody, Mass.

Process of Making Leather-Board. U. S. Patent No. 981,591. ALBERT L. CLAPP, Braintree, Mass.

Belt-Stretcher. U. S. Patent No. 979,599. FREDERICK THOMAS, London England.

Clarifying Extracts Containing Tannin. U. S. Patent No. 979,656. HERMANN DAMKOHLER AND HUGO SCHWINDT, Bremen, Germany.

The process consists in adding to the extract barium meta-aluminate and precipitating the resulting color-lake by means of a water-soluble sulphate.

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Apparatus for the Sterilization of Water and Other Liquids. U. S. Patent No. 979,999. CASMIR STANISLAUS PIESTRAK, Paris, France.

The method employes air, which has been ozonized by passing through an annular space between two electrodes carrying a suitable electric current.

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Journal of the

American Leather Chemists' Association

Vol. VI MARCH, 1911 No. 3

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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ACTIVE.

Max F. Woltz, Salem, Virginia.

TESTS FOR ESTIMATING THE PURITY OF COMMERCIAL CHESTNUT OAK BARK EXTRACTS.

By Fritz H. Small.

The purpose of this article is to describe briefly certain tests which have been used by the writer and his assistants in the laboratory of the Graton & Knight Mfg. Co. for estimating the

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purity of commercial chestnut oak bark extracts. The tests are not original with the writer save in the manner of use. The figures are original and may prove of assistance to any one who is at work on the problem stated above.

While some rather skilful counterfeits of a chestnut oak bark extract have been made by mixing various foreign and native tanning materials, the usual chestnut oak bark extract in the domestic market is pure except for a possible admixture of chestnut wood extract or of extract from other oak barks than chestnut. The oak barks sometimes used are red, Spanish, water, and rarely black. The investigation of the extract to determine which, if any, of these latter materials are present will usually show whether a more complex mixture is being studied.

It may be stated at the outset that the writer was much disappointed in his study of this problem to find as his investigations progressed that there is as much variation among different specimens of genuine chestnut oak bark as among different specimens of genuine Newfoundland cod livers. Because of this variation it seems improbable that an exact determination of the amount of chestnut oak bark tannin in a mixed extract of even so simple a composition as a mixture of chestnut oak bark and chestnut wood extracts can be attained,—much more improbable if the mixture is more complex. On the other hand while the variations in individual samples of chestnut oak bark are considerable, the average pure chestnut oak bark extract of commerce runs through a rather small range of values and if fairly consistent in its reactions and constants. It must be understood, therefore, that the results given below are for average samples, and that while these are the results to be expected, individual specimens may show quite other.

To be able to make satisfactory comparisons by qualitative tests it is essential that the tests be made under as nearly as possible the same conditions. The procedures described are those which the writer has found best. In all cases analysis solutions of as nearly as practicable 0.4 gms. tannin to 100 cc. were used. Inasmuch as the qualitative reactions are apt to be altered by the age and condition of the solution tested, it is desirable always

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to work with a fresh analytical solution. Following are some of the qualitative tests which the writer has found helpful:—

Sulphuric Acid Test[1]:—Put three drops of solution in a test-tube; run in down the side 1 cc. of concentrated sulphuric acid; shake gradually until a uniform color is obtained; note color. Dilute with 3 cc. of water; note color and precipitate.

Ferric Ammonium Alum Test[2]:—Dilute ⅔ cc. of solution to 10 cc. and add one drop of a 1 per cent. solution of ferric ammonium alum,—test-tube. Note color and formation of precipitate.

Ammonium Acetate Test[3]:—Add concentrated acetic acid to concentrated ammonia till slightly acid. To 10 cc. of solution in a test-tube add 5 cc. of the ammonium acetate solution obtained above, and let stand one hour; note formation of precipitate. Boil and note precipitate.

Lime Water Test[4]:—To 10 cc. of solution in a test-tube add 5 cc. of lime water; shake and allow to stand undisturbed for twenty-four hours; note color of precipitate, and color of clear top solution by both reflected (fluorescence) and transmitted light.

	C. O. bark	Red oak	Black oak	Spanish oak	Water oak	Chestnut wood
H_2SO_4 con.....	crimson	crimson	reddish yellow	brown	brown	yellow
dil.	pink	pink	yellow	brown	yellow brown	yellow brown
$Fe_2(NH_4)_2(SO_4)_4$.	green	green	green	blue	blue	blue
$(NH_4)C_2H_3O_2$ cold	pr.	pr.	pr.	pr.	pr.	pr.
boil	clears up	clears up	clears up	remains in part	remains in part	much remains
CaO_2H_2	crimson	crimson	crimson	straw	straw	green

These tests will serve to show the probable purity of the extract and give an idea of the nature of the foreign materials present.

To estimate the probable extent of the impurities the writer

[1] Procter, L. I. L. B., Chap. VIII.
[2] Procter, L. I. L. B., Chap. VIII.
[3] Communicated to writer in a letter by A. W. Hoppenstedt.
[4] Procter, L. I. L. B., Chap. VIII.

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has found the formaldehyde-hydrochloric acid method[1] of Stiasny most helpful. Stiasny has shown that the reaction does not separate quantitatively the pyrogallol and catechol tannins. In the writer's experience, however, the method can be so used as to give a constant weight of precipitate from a given solution. When so used moreover it will be found that if two solutions be mixed, the precipitate-weight of the mixture will be that calculated from the precipitate-weights of the components. After some months of experimenting the following procedure was settled upon as yielding the sharpest differentiation of materials and most consistent results.

Prepare a 2 per cent. solution of formaldehyde and a ½ per cent. solution of hydrochloric acid. Mix these in equal volumes (1-1) immediately before use.

Prepare a solution of the extract to be tested as for analysis, making it to contain as nearly as practicable 0.4 gms. tannin to 100 cc. Filter this solution as for a soluble-solids determination by the official method and obtain 160 cc. or more of clear soluble-solids filtrate.

To 50 cc. of the clear soluble-solids filtrate in a crystallizing dish add 50 cc. of the mixed formaldehyde-hydrochloric acid solution. To 100 cc. of clear soluble-solids filtrate in a 250 cc. graduated flask add 100 cc. of the mixed formaldehyde-hydrochloric acid solution. Cover the crystallizing dish with a watch-glass to prevent evaporation and place both it and the flask on adjacent openings of a steam bath. Heat with a good flow of steam for 2½ hours; remove; allow the flask to cool one hour in the air, then cool with water at approximately 20° C to 20° C and make up to the mark. Filter this solution as for a soluble-solids filtration by the official method, discarding the 75 cc. of liquor used for digestion, and collecting for use only when the filtrate comes clear.

Pipette 125 cc. of the clear filtrate into a crystallizing dish and evaporate both it and the solution in the other crystallizing dish, to which 25 cc. of water has been added, to dryness on a steam bath. (Because of hydrochloric acid fumes the combined evaporator and dryer must not be used for this evapora-

[1] *Der Gerber*, 1905, p. 186; *Collegium*, 1908, p. 419.

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tion.) Transfer to the combined evaporator and dryer and dry for 16 hours; put in desiccators, cool, and weigh. These weights should be corrected for any variation from 0.4 gm. tannin to 100 cc. in the strength of the original solution.

A series of tests of various mixtures of wood and bark liquors by this method gave results as follows:—

	Wt. of total	Wt. of filtrate	Precip.-wt. found	Precip.-wt. calculated
Bark No. 1	0.3553	0.2010	0.1543	..
Wood	0.2731	0.2581	0.0150	..
1 bark No. 1, 3 wood	0.2946	0.2435	0.0511	0.0499
2 bark No. 1, 2 wood	0.3140	0.2286	0.0854	0.0847
3 bark No. 1, 1 wood	0.3339	0.2166	0.1173	0.1195
Bark No. 2	0.3255	0.1559	0.1696	..
1 bark No. 2, 2 wood	0.2871	0.2203	0.0668	0.0666
3 bark No. 2, 1 wood	0.3138	0.1798	0.1340	0.1310

The average precipitate-weight of the usual chestnut wood extract by this method is not far from 130. Results from various samples of chestnut wood extract are as follows:—122, 118, 124, 135, 141, 138, 146, 150. The average precipitate-weight of chestnut oak bark extract is above 1,600. A great many tests of chestnut oak bark extracts and of chestnut oak barks have been made in this laboratory and a succession of values from the note books may be recorded here:—1878, 1610, 1840, 1866, 1678, 1709, 1818, 1725, 1889, 1757, 1623, 1543, 1553, 1615, 1640, 1644, 1658, 1690, 1760, 1660, 1826, 1717, 1652, 1604, 1630, 1777, 1741, 1737, 1520, 1661, 1684, 1673, 1753, 1733, 1688.

Opportunity has been found in this laboratory up to the present to test comparatively few specimens of other oak barks than chestnut. A test of a series of samples of red, Spanish and water oak barks furnished the writer by Mr. G. A. Kerr, and of black oak bark furnished the writer by Mr. H. C. Reed gave results as follows:—

	Analysis			Wt. of	Wt. of	Precip.
Kind	Sol. sol.	Non-tan.	Tannin	total	filtrate	weight
Red	11.09	4.28	6.81	0.3298	0.1661	0.1637
Black	14.24	5.68	8.56	0.3409	0.1516	0.1893
Spanish	14.32	7.78	6.54	0.4316	0.2864	0.1452
Water	7.70	4.43	3.27	0.4773	0.3665	0.1108

It will be noticed that while the results of the tests made by this method on different samples of chestnut oak bark and chest-

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nut oak bark extract show a considerable variation, none of the precipitate-weights found are below 1,500. Owing to the fact that this variation exists in samples of undoubted genuineness, the impossibility of establishing a standard precipitate-weight for chestnut oak bark is evident. Inasmuch, however, as the results of the many tests of chestnut oak barks and chestnut oak bark extracts made in this laboratory during the past year have discovered no genuine chestnut oak bark extract which gave a precipitate-weight below 1,500,—it may be stated with very small likelihood of error that any extract tested by this method which shows a precipitate-weight of less than 1,500 is not a pure chestnut oak bark extract. In the same way in estimating the percentage composition of mixtures of chestnut oak bark and of chestnut wood extracts, if 1,500 be assumed for the precipitate-weight of chestnut oak bark and 130 for the precipitate-weight of wood, and the percentage composition of the mixture be calculated from these values and from the precipitate-weight of the mixture as found, it is certain with little chance of error that the calculated percentage gives the extract credit for all the chestnut oak bark extract likely to be present.

It is manifestly impossible in an article of this sort to explain in detail all the applications of the method. While its usefulness for testing the purity of chestnut oak bark extract has been suggested in this article, the principle and method are of much wider application and it only needs the establishing of a series of values for different materials to enable one to estimate more accurately than by any other method known to the writer the percentage composition of a mixture, the components of which are known, or otherwise, to assist him in the determination of the nature of the components in an unknown mixture.

THE USE OF CASEIN IN DETERMINING TANNIN.

M. Nierenstein.

(*Chemiker Zeitung*, No. 4, 1911, p. 31.)

In the year 1903, at the suggestion of Dr. T. Körner, at that time an instructor in the German Tanning School in Freiberg, Saxony, I experimented on the use of casein as an agent for

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detannization in the analysis of tanning materials. Since that time, through my own work and that of E. Drabble, D. Spence, H. E. Roaf,[1] T. A. Webster and L. R. Thompson I am convinced of the trustworthiness of this method for the estimation of tannin in barks and fruits. On the whole we have carried out from 750 to 800 analyses. The values so obtained were from 1 to 1.5 per cent. higher than those by the hide-powder method.

Our method is not adapted to the analysis of tanning extracts, because the decolorized extracts often contain aluminum oxide, which the casein dissolves, thus causing the figures for the non-tannins to come out too high.

Recently I had occasion to discuss with Prof. Dr. E. Knecht the analysis of tannins in the dyeing industry, and mentioned among others this method also, which was as yet unpublished. The possible importance of the method for the textile industry induces me now for the first time to make it public.

We employed for the analyses Kahlbaum's casein, carefully freed from fat by extraction with ether, according to Hammarsten, 100 cc. of the tan-liquor were shaken for 10 minutes with 6 gr. of casein, and then treated with 3 more grams of casein and filtered. Then we proceeded as in the hide-powder method. The following are test analyses performed on Schering's pure levigated tannin.

5 g. tannin dissolved in 500 cc. water gave for 50 cc.

I.		II.	
Total solids..	0.4982 g.	Total solids..	0.4986
Non-tans	0.0014 g.	Non-tans	0.0010
Tannin	0.4968 g. = 99.36%	Tannin	0.4976 = 99.52%

5 g. tannin and 5 g. gallic acid in 1000 cc. water; 50 cc. gave

I.		II.	
Total solids..	0.4988 g.	Total solids..	0.4998
Non-tans	0.2496 g.	Non-tans	0.2478
Tannin	0.2496 g. = 49.8%	Tannin	0.2520 = 50.4%

5 g. tannin and 5 g. glucose in water; 50 cc. gave

Total solids..	0.4994
Non-tans	0.2476
Tannin.....	0.2518 = 50.36%

[1] Dr. H. E. Roaf made the interesting observation that casein which has been acted on by tannin does not give the Millon reaction. This observation tends to support my hypothesis that tannage is accompanied by chemical processes.

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I have already[1] reported on a series of quantitative estimations of sugar in tanning solutions which had been detannized by means of casein, so that I omit further sample analyses. From the instances cited it is evident that casein absorbs tannin quantitatively, while it does not take up gallic acid nor glucose, which so often accompany the tannins.

THE EMPLOYMENT OF THE ELECTROMETRIC METHOD FOR THE ESTIMATION OF THE ACIDITY OF TAN LIQUORS.[2]

PART I.

By Henry J. S. Sand, PH.D., D.SC., and Douglas J. Law, B.SC., F.I.C.

The determination of the acidity of tan-liquors is a matter which is at the present time undergoing a considerable amount of discussion. This is due not only to the difficulty of finding indicators which give a plain color-change in the dark liquids to be titrated, but more still, to the uncertainty which has prevailed in the minds of tanners as to an exact definition of the terms acid, alkaline, and neutral. We may say that apart from the ionic theory, no attempt ever has been made to fix these ideas in an objective manner. It is a commonplace that different indicators will turn at entirely different points when such weak acids as occur in tan-liquors are present, and also that the degree of acidity on which a property such as swelling power depends cannot be simply expressed by stating the equivalent concentration of the acid. As is well known, the ionic theory affirms that degree of acidity depends on the concentration of hydrogen ions, a strongly acid solution being one in which the hydrion concentration is great, an alkaline solution, one in which it is extraordinarily minute, and if we wish to adopt absolutely pure water as our standard of neutrality, a neutral solution is one in which the hydrion concentration is approximately 10^{-7} normal. The ionic theory also furnishes us with a direct means of estimating hydrion concentration, and this means consists in

[1] M. Nierenstein, *Chem. Zeitung*, 1909, p. 15.

[2] *Journal of Society of Chemical Industry*, Jan. 16, 1911.

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measuring the difference of potential between that liquid and a hydrogen electrode. Other methods for the same purpose must obviously be as numerous as are the functions of hydrogen-ion concentration, but more particularly for the determination of small hydrion concentrations, the electrometric method is the most direct, and has in most cases served to standardize the others. Of the subsidiary methods that of indicators is by far the most important, and owing to the researches of Friedenthal (Zeits. Elektrochem. 1904, **10**, 113; *ibid.* 1908, **14**, 125); Salessky (Zeits. Elektrochem. 1904, **10**, 204); Fels (Zeits. Elektrochem. 1904, **10**, 208); Salm (Zeits. Elektrochem. 1904, **10**, 344. Zeits. Phys. Chem. 1907, **57**, 471); Sörensen (Sur la mésure et l'importance de la concentration des ions hydrogène dans les reactions enzymatiques. Comptes Rendes Laboratoire de Carlsberg, 1909, **8**, 1); and others, we now possess a whole range of indicators which have been standardized in such a manner that it is possible to select one or more, to indicate almost any arbitrarily fixed hydrogen ion concentration. For the investigation of tan liquors, however, only a small fraction of these is available owing to the deep color of the solutions to be titrated; and the turning points of this fraction do not necessarily correspond to a hydrion concentration which is of importance to the tanner. The electrometric method, on the other hand, allows any arbitrarily fixed hydrion concentration to be determined, and it was this consideration which led Mr. J. T. Wood to suggest to us the desirability of testing the electrometric method, more especially in order to examine its practicability for determining the original hydrion concentration of a tan liquor and also the amount of alkali which must be added until a hydrion concentration corresponding to the turning point of some well recognized indicator such as particularly phenolphthalein, is reached. There is reason to believe that the former is an essential factor on which the swelling power of the liquor depends, and that the latter will be connected with its capacity for dissolving lime (see table 2). The present results are of a preliminary nature, and are given with a view to show the general practicability of the method, and in response to repeated requests that we should publish a complete and coherent account of the form in which

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the electrometric process is employed by us. This method of titrating acids and alkalies was first put forward by Böttger (Zeits. Phys. Chem., 1897, 24, 253) working in Ostwald's laboratory in 1897, and may be said to depend on the fact that when metals and also hydrogen absorbed by platinum black, are brought in contact with solutions which contain these same substances in the ionised condition, a potential difference is established which depends, not only on the nature of the substances in contact, but also, on the concentration of the ions in solution. In the form in which the method was described by Böttger, it could however hardly be employed in the titration of the weak acids occurring in tan-liquors. It is generally believed that the complication of apparatus required for carrying out estimations of this sort is so great as to render the method unsuitable for practical purposes. We have found however, that when the auxiliary electrode and a potentiometer-box devised by one of us for the purpose of the separation of metals by graded potential (Sand. Trans. Faraday Soc., 1909, 5, 159; Trans. Chem. Soc., 1907, 91, 373, and 1908, 93, 1572) are employed, the method becomes easy and certain of application, and all the apparatus may be set up in a few minutes.[1]

Apart from the beaker containing the liquid to be examined and a burette for delivering alkali into it, the apparatus consists of the hydrogen electrode and the auxiliary electrode, both dipping into the liquid; and the potentiometer box for measuring the difference of potential between them.

The accompanying figure shows the hydrogen electrode I. and the auxiliary electrode II., drawn to scale, on the right, whereas the electrical apparatus is explained diagrammatically on the left.

We are at present engaged in examining various forms of hydrogen electrode in order to find which is the most suitable for our purpose. The one shown in the figure has been improvised for the experiments recorded here, and we therefore describe it, but do not on this account wish to put it forward as the best form available. It will be seen that it consists essential-

[1] The apparatus was made partly by Universitätsmechaniker Fritz Köhler, of Leipzig, and partly by Messrs. Griffin, of London.

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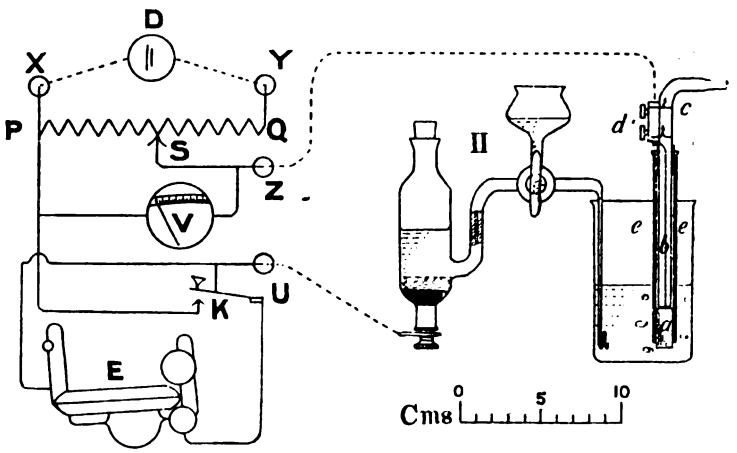
ly of a thin platinum plate, *a*, which is fastened to a long thin platinum wire, *b*. The latter is fitted inside the glass tube, *c* and is sealed through it near the top, and then ends in the terminal, *d*. The plate, *a*, is surrounded to within about 2 mm. from the bottom by the glass tube, *e*, which is fitted to *c* by a piece of rubber. The hydrogen escapes through the liquid at the bottom. The whole apparatus is suspended by means of a piece of string from a ring fitted on the burette-stand in such a manner that it may be employed for stirring the liquid, but cannot come in contact with the bottom of the beaker. The



platinum plate, *a*, is coated with platinum black by the Lummer Kurlbaum method, *i.e.*, by making it the cathode in a 3 per cent. solution of platinum chloride containing one-fortieth per cent. lead acetate, the current being regulated so as to produce a moderately vigorous evolution of hydrogen. A single coating has lasted for more than fifty titrations. Hydrogen obtained by the action of hydrochloric acid on zinc and purified by means of alkaline permanganate solution enters at the tube, *c*, and escapes at the bottom. The initial saturation of the platinum black requires a passage of the gas for 25 to 30 minutes. When once saturated, however, the transference of the electrode from one liquid to another occasions no loss in saturation greater than

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can be remedied by allowing the hydrogen to pass for about one minute before proceeding with the titration.

The auxiliary electrode-vessel, II., will require little further explanation. For our purposes in which an accuracy of about one centivolt is sufficient, we believe that the normal calomel electrode is the most suitable. This electrode was made up according to the directions given by Ostwald-Luther's Handbuch[1] and not exposed unnecessarily to light. The left limb of the capillary connection is filled from the funnel with normal potassium chloride solution, whereas the other limb contains a 3.5 normal solution of the same substance. It is known that the diffusion-potential between this solution and the other solutions of small concentration is always small. In those cases in which Bjerrum (Zeits. Phys. Chem., 1905, **53**, 428), succeeded in determining such diffusion potentials, they did not exceed one centivolt. During use, the tap of the electrode, which must be maintained free from grease, is kept closed, the layer of liquid held by capillary attraction around the barrel forming the connection.

One of the most important points in every method of titration is what may be called the end-reaction. In the present case we have to decide which potential-difference between the calomel and the hydrogen electrode is to be taken as an index that the titration is complete. If the object of the titration be to estimate the number of equivalents of acid present, then this potential-difference can only be determined if it is known which is the acid present and what is the concentration of the sodium salt resulting from the titration.[2]

We have not gone into this matter fully as yet, and it is by no means certain that an end-reaction resulting from considerations

[1] Some pure mercury is poured into the electrode vessel. On this a layer of about 1 cm. in height is poured of a paste made by shaking up mercury very thoroughly with calomel in a normal potassium chloride solution, pouring off the supernatant liquid and repeating the operation several times. Finally the vessel is charged with a normal solution of potassium chloride, which has been thoroughly saturated with mercurous chloride by shaking up with the above paste.—For a discussion of the sources of error in this electrode see Coggeshall. *Zeit. Phys. Chem.*, 1895, 17, 63.

[2] For a discussion of this matter see Salm und Friedenthal, *Zeit. Elektrochem.*, 1907, 13, 125.

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of this kind would be of special importance to the tanner. In the meantime we have adopted the value 0.69 volt as our end-voltage. This number was obtained primarily by running a $N/10$ soda solution into a $N/10$ acetic acid solution containing phenolphthalein until the first indication of pink was observed. At the dilution of this experiment the change of color very nearly corresponds to the point at which the base has been added in a quantity equivalent to the acid originally present. The value 0.69 volt also corresponds very nearly to a hydrion concentration equal to that of pure water as is shown by the following considerations.

Taking the potential difference between a normal calomel electrode and a hydrogen electrode placed in contact with hydrions of normal concentration to have the value given by Wilsmore (Zeits. Phys. Chem., 1900, **35**, 302) of 0.283 volt, then Nernst's formula leads to the corresponding P. D. (π) for a hydrion concentration C. at 17° of

$$\pi = \left(0.283 + 0.0575 \log \frac{1}{C}\right) \text{ volt} \ldots \ldots \ldots (1)$$

For a hydrion concentration C. of 10^{-7}, corresponding approximately to pure water, this leads to $\pi = 0.283 + 0.403 = 0.69$ volt. Similarly, by the employment of a new method, Lorenz and Mohn (Zeit. Phys. Chem., 1907, **60**, 422), arrived at the value 0.75 volt for the potential difference between a $N/10$ calomel electrode and a hydrogen electrode placed in an accurately neutral liquid. This would correspond to a voltage between 0.69 and 0.70 if a N calomel electrode had been employed. Our results thus lead to the conclusion that phenolphthalein begins to change color at a hydrion concentration of 10^{-7} normal. This value agrees with that given by Salessky (Zeit. Elektrochem, 1904, **10**, 204) but is greater than that of Friedenthal (*ibid.* p. 117) and Salm (Zeit. Phys. Chem., 1906, **57**, 471).

The potentiometer-box already referred to is employed for measuring the potential-difference between the calomel and the hydrogen electrode. The principle of the method of measurement consists in connecting the two ends, P and Q, of a sliding rheostat to the terminals of a dry cell, D, and balancing the potential-difference to be measured against the potential-differ-

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ence between one end, P, and the slider, S, by means of a special form of enclosed capillary electrometer, E. The value of this potential-difference is read directly on a delicate voltmeter, V. The connections, which are found ready-made in the box, have been drawn out, whereas those to be made by the operator are shown by dotted lines. The steps to be taken by the latter consist first in taking off the capillary electrometer and manipulating it in such a manner that on returning it into position the capillary may be partly filled with a thread of mercury and partly with the acid. The terminals, X and Y, marked battery + and —,are connected to a dry cell, and the terminals, Z andU, marked cathode and auxiliary respectively, to the hydrogen and the calomel electrode. Very careful insulation of the connection between the terminal marked auxiliary and the calomel-electrode is necessary. The hydrogen is passed through the hydrogen electrode until a constant P. D. between it and the calomel electrode is obtained. This P. D. is measured by moving the slider up and down until no movement of the mercury in the capillary electrometer is observed on depressing the key K marked electrometer. In carrying out this operation care must be taken not to touch any bare terminals or wires with the hand, as false earth connections may otherwise be introduced. The key should be depressed long enough to allow the mercury to move; we have had occasion to observe that many operators have an exaggerated idea of the liability the instrument might show to become polarized. The initial P. D. is then read directly on the voltmeter on the scale ranging from 0 to 1.5 volt.[1] As already stated, this measures the original hydrion concentration of the liquid which there is reason to believe bears some relation to its swelling power. Alkali is then run in until, after equilibrium has been established, the voltmeter shows 0.69 volt, when the liquid is assumed to have been neutralized. When a hydrogen electrode is employed which has been saturated before the beginning of

[1] NOTE.—The potentiometer-box as used for purposes of electro-analysis contains in addition to the apparatus and terminals shown in the diagram, a terminal and a tapping key, both marked anode. When the latter is depressed the voltmeter reads directly the difference of potential between the terminals "anode" and "cathode" on a second scale ranging from 0 to 6 volts.

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the experiment, a titration usually occupies about three minutes. The initial reading of the voltmeter during the titration of the tan-liquors which we have examined was usually found to be about 0.54 volt, which, according to equation (1), corresponds to the value;

$$x = \log \frac{1}{C} = \frac{1}{0.0575}(0.54 - 0.283) = 4.5.$$

Following the example of Sorensen (*loc. cit.*) we may call x the exponent of the hydrogen-ion concentration and may conveniently employ it to measure the smallness of the acidic action of our solution.

The readings of the voltmeter may be checked from time to time by means of a Clark or Weston cell connected to the terminals, cathode and auxiliary. If the volt-meter has been fitted in a hermetically sealed case, and mounted on rubber, there is little reason to apprehend that its readings will become untrustworthy. The instrument employed by us has been in use for about two years without showing any error.

The method was checked by first titrating a tan-liquor electrometrically with $N/10$ alkali and then adding known quantities of $N/10$ acetic, lactic, or butyric acid to the neutralized liquids and titrating again. The acids had been standardized previously against $N/10$ soda by means of phenolphthalein. The following are typical results (table 1).

TABLE I.

Acid : Acetic		Lactic		Butyric	
Cc. added	Cc. found	Cc. added	Cc. found	Cc. added	Cc. found
5	4.9	5	5.0	9.9	9.85
10	9.9, 10.0, 10.05	10	9.90, 9.95, 9.90	14.85	14.75
15	15.1	15	15.08, 15.05	..	..

Table 2 gives a comparison between the acidity of various liquids determined electrometrically on the one hand and by Procter's lime-water method on the other.

TABLE II.

Cc. N/10 Alkali Required to Neutralize 10 cc. of the Liquors.

No.	1	2	3	4	5	6	7
Electrometric ..	7.0	9.1	10.0	10.6	10.3	10.45	10.65
Lime-water	5.88	8.24	8.75	9.4	9.03	9.40	9.26

We hope shortly to be able to make definite proposals as to the

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most suitable form of hydrogen electrode and to be in a position to discuss more fully the information which may be derived from the different potentiometer readings, more particularly in its bearing upon questions affecting the tanning of leather. We trust, however, that the preceding account may be of use to anyone wishing to employ the method in the meantime and may prove, that when carried out with the means at present at our disposal, the method is both simple in application and certain in its results.

A NEW METHOD OF ESTIMATING CHROMIUM.[1]

During the last decade chrome tannage has satisfactorily developed in England. This is due to the researches of Professor Procter, who, in the year 1897, published freely and without patent, or payment, a new method of producing single-bath chrome liquor by the reduction of bichromate with sugar or glucose, and in 1898 a second for the use of chrome alum. We have now about 10 different kinds of "one-bath" chrome liquor in the market, made on the same principles. For the sake of economy, as well as for the satisfactory tannage, analytical control of the various processes now in vogue is absolutely necessary. In one-bath chrome liquor what is usually required is the concentration and basicity of the solution, *i.e.*, the strength in chromium and the amount of the acid radical combined with it. Chromium in the liquor can be estimated in several ways, either by gravimetric or by the volumetric methods; but the former is elaborate and long, and is likely to tax the patience of the experimenters. Of the volumetric methods two are most commonly employed according to the nature of a liquor. These are the "peroxide method," using sodium peroxide as an oxidizing agent, and the "fusion method" whereby the dry residue of chrome liquor is oxidized with the fusion mixture, consisting of sodium carbonate and magnesium oxide in equal proportions. The "fusion method" is comparatively much slower and is more suited to the estimation of chromium in leather. The peroxide method is quicker, no doubt, but not without some difficulty. Sodium peroxide is dangerous and requires careful manipulation. When

[1] *The Leather Trades Review.*

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the reagent is added to the liquor a large amount of oxygen is evolved, causing a brisk effervescence; so that, unless the beaker is quickly covered, there is always liability of a certain loss by spurting. Besides, special precaution and constant watching are necessary when the mixture is heated to destroy the excess of peroxide. The writer, in course of his investigations on "two-bath" chrome tannage, while oxidizing with alkaline bromine sodium tetra-thionate in a solution containing the sulphates and the chlorides of chromium (the products of the second bath) discovered the formation of yellow chromate. This led him to think of employing alkaline bromine instead of peroxide. After repeated experiments on one-bath chrome liquor he found the following method as satisfactory as any other, and at the same time free from much trouble:—

Prepare the reagent by addition of bromine water in slight excess in a saturated solution of caustic potash. A liter of this reagent is quite sufficient for 40 different experiments. A quantity of liquor to contain 0.3 to 0.5 gms. of chromium is measured into a rather large beaker and diluted (if necessary) to 100 cc. with distilled water. To this add solution of KOH, which is kept as a laboratory reagent, till the precipitate re-dissolves. Then 25 cc. of the reagent are added to it, and the beaker is placed on the steam-bath to warm. Ten to 15 minutes warming is enough for complete oxidation. Leave the beaker for another 15 minutes on the bath to drive off the excess of bromine, which is much facilitated by the addition of dilute HCl. If the used liquor is to be analyzed destroy the organic matter contained therein by boiling it with 5 cc. of strong HNO_3 before adding the reagents. Sufficient HCl is added to the chromate solution for the complete liberation of the bichromic acid, from which chromium is estimated in the usual way by means of $\frac{N}{10}Na_2S_2O_3$, and starch in presence of 10 per cent. solution of potassium iodide. The reactions may be represented by the following equations:—

$$Cr_2(SO4)_3 + 6KOH = 2Cr(OH)_3 + 3K_2SO4.$$
$$Cr(OH)_3 + 3KOH = Cr(OK)_3 + 3H_2O.$$
$$2Cr(OK)_3 + 4KOH + 3Br_2 = 2K_2CrO_4 + 6KBr + 3H_2O.$$

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The results of four experiments along with those found by some standard methods, are given in the following table in terms of the quantity of $\frac{N}{10}$ $Na_2S_2O_3$ required in each case.

For 25 cc. of the different solution	1	2	3	4
Using Na_2O_2.....	17.5 cc.	15.85 cc.	19.6 cc.	14.35 cc.
Using Alkaline Br ...	17.6 cc.	15.8 cc.	19.6 cc.	14.3 cc.

THE ECONOMIC POSSIBILITIES OF THE MANGROVE SWAMPS OF THE PHILIPPINES.[1]

By Raymond F. Bacon and Vicente Q. Gana.

In the United States, and in other countries where large amounts of leather are manufactured, the forests yielding native tanning materials have been so far exhausted that these nations must look to other countries for their source of supply. At the present time very large quantities of tan barks and cutch are imported into the United States from Borneo, Dutch East Africa, Brazil and other tropical countries, and the use of mangrove tanning materials is constantly increasing. The most abundant source of tanning substances in the Philippines is the mangrove swamps of the Islands. At the present time there is no mangrove bark exported from the Philippines, and as yet the area of these swamps is not known. They occur as narrow fringes along the coast or in considerable areas at the mouths of large rivers, especially at the head of bays. Some limited areas have been mapped and measured by the Forestry Bureau. These are as follows:

(1) Island of Mindoro, about 10,000 hectares, which will yield approximately 50,000 tons of bark.

(2) The east coast of the Zamboanga Peninsula, Mindanao, contains about 9,000 hectares of mangrove swamp; this will yield at least 90,000 tons of bark, found on a coast line about 45 miles in length. In the same region, on the other side of the Gulf of Subuguay, there are probably 9,000 hectares more which will also yield at least 10 tons per hectare. With the exception of a number of areas of 1,000 hectares or less, no fur-

[1] Condensed from the *Philippine Journal of Science*, Vol. IV, No. 3.

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ther regions have been examined carefully. The above statement gives a very small proportion of the total area of the mangrove swamps. It is believed that the swamps of Mindanao alone will yield enough bark to furnish a continuous supply to a very large cutch factory.

The tan barks of Mindanao average from 23 to 25 per cent. of tannin, and these are the best that have thus far been examined from the Islands. Such bark could not be profitably shipped to the United States to compete with the East African barks carrying 50 per cent. of tannin. A careful analysis of conditions shows that the only method of handling the tan barks commercially is by means of an extract factory at the source of supply and it appears that such a factory could be operated very profitably with free trade between the Philippines and the United States

All the species of mangrove trees of the eastern tropics, which are used commercially for tanning purposes, are also found in the Philippines. These are:

Rhizophora mucronata Lam.
R. conjugata L.
Bruguiera gymnorhiza Lam.
B. eriopetala W. & A.
B. parviflora W. & A.
B. caryophylloides Blume.
Ceriops tagal (*Perr.*) C. B. Robinson.

There are three large cutch factories in Borneo using tan barks from the same species of mangrove as those found in the Philippines.

Tables of analyses made on mangrove tan barks are given below. It will be noted that the barks from Mindanao run very much higher in tannin than those from Mindoro, and it has often been observed that, as the equator is approached, the tannin percentage increases. The analyses below were made by the methods of the International Leather Chemists Association, using the American "shake modification." As our machine does not give very violent shaking and as we have used unchromed hide powder, it is possible that our results may be as much as 2 per cent. low. We are now taking measures to standardize our

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analyses with those made by a recognized leather chemist and in a subsequent communication will report several hundred analyses of mangrove tan barks from the southern islands, so that perfectly reliable data will be at hand for possible investors in this field.

TABLE I.—ANALYSIS OF BARKS FROM PORT BANGA, ZAMBOANGA.

Forestry Bureau No.	Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bark: Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
9,356	2,056	Tabique	*Xylocarpus obovatus* A. Juss	14.9	69.7	30.3	8.6	21.7
9,357	2,057	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.4	65.2	34.8	11.6	23.2
9,358	2,058	Bacauan	*Rhizophora mucronata* Lam	14.4	61.7	38.3	12.4	25.9
9,359	2,059	Pototan	*Bruguiera parviflora* W. & A.	13.9	84.1	15.9	7.1	8.8
9,360	2,060	Pototan	*Bruguiera gymnorrhiza* Lam	16.1	63.0	36.96	9.8	27.2
..	..	Tabique	*Xylocarpus obovatus* A. Juss	14.2	67.6	32.4	7.7	24.7

These barks were collected on Jan. 1908 by Dr. H. R. Whitford and W. I. Hutchinson from Port Banga, Zamboanga. They are rather large quills with thick, harsh, dirty brown scales on the outer surface. Tabique gave a very dark, red infusion; tangal a somewhat light red infusion; bacauan gave an intense red infusion. Pototan (*Bruguiera parviflora*) is a fibrous bark difficult to grind; it gave a red infusion. Pototan (*Bruguiera gymnorrhiza*) gave the same grind; it gave a red infusion. Pototan (*Bruguiera gymnorrhiza*) gave the same colored infusion as the previous one.

The barks were collected by Mr. M. L. Merritt in Mindoro in March, 1908. Bacauan bark is brittle and is very easily ground. It has a dirty brown scale of variable thickness which is very easily removed from the true or inner bark.

Analyses were made on both entire and inner bark of each variety. In every case inner bark showed a higher percentage of tannin than when entire bark was assayed.

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TABLE II.—Analysis of Barks from Mindoro.

Forestry Bureau No.	Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bath			
					Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
9,779	1,911	Bacauan	*Rhizophora conjugata* L.	13.2	67.4	32.6	12.0	20.6
9,780	1,912	Bacauan	*Rhizophora conjugata* L.	14.4	66.6	33.4	10.7	22.7
9,781	1,913	Hangalay	*Bruguiera parviflora* W. & A.	14.0	77.4	22.4	9.6	12.8
9,782	1,914	Pototan	*Bruguiera gymnorrhiza* Lam	13.9	60.2	39.8	11.6	28.2
[1]9,783	1,915	Bacauan	*Rhizophora mucronata* Lam	13.2	64.3	35.7	14.1	21.6
9,795	1,921	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	11.8	69.1	30.9	9.7	21.2
9,816	1,922	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.3	72.5	27.5	10.5	17.0
9,851	1,984	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.7	71.5	28.5	8.0	20.5
[1]9,780	1,912	Bacauan	*Rhizophora conjugata* L.	13.5	64.8	35.2	10.8	24.4
..	1,912½	Bacauan	*Rhizophora conjugata* L.	14.1	67.1	32.9	10.0	22.9
..	[1]1,913½	Hangalay	*Bruguiera parviflora* W. & A.	14.8	75.5	24.5	9.6	14.9
..	1,913¾	Hangalay	*Bruguiera parviflora* W. & A.	12.9	82.1	17.9	8.3	9.6
..	1,914½	Pototan	*Bruguiera gymnorrhiza* Lam	13.9	63.4	36.6	12.6	24.0
..	[1]1,915½	Bacauan	*Rhizophora mucronata* Lam	13.4	67.1	32.9	15.1	17.8

Bacauan numbered 1,912 contained approximately 10 per cent. outer scale.

Bacauan infusions were red, but varied in intensity.

The Hangalay barks are reddish-brown in color with rough, dark brown scales.

The inner bark of Hangalay is fibrous and the ground bark was very irritating to the mucous membranes of the nose and throat when inhaled. They also gave red infusions.

[1] Analysis of inner bark.

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Barks of Pototan and Tangal also possess rough, brownish scales.

The infusions were somewhat lighter than those of Bacauan.

TABLE III.—ANALYSIS OF BARKS FROM PORT BANGA, ZAMBOANGA.

Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bark: Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
11,534	Bacauan	*Rhizophora conjugata* Lam	13.4	68.7	31.3	13.3	18.0
11,535	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	11.9	58.6	41.4	19.1	22.3
11,536	Pototan	*Bruguiera gymnorrhiza* Lam	13.5	62.0	38.0	13.5	24.5
11,537	Lañgaray	*Bruguiera parviflora* W.& A.	13.8	80.4	19.6	8.0	11.6

This table shows results of analysis made on another lot of barks from Port Banga, Zamboanga, collected by H. N. Whitford on December, 1908.

TABLE IV.—ANALYSIS OF MANGROVE BARKS FROM SARAWAK, BORNEO.

Common name	Scientific name	Moisture (per cent)	Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
Gayong	*Rhizophora mucronata* Lam	14.4	70.1	29.9	9.4	20.5
Bakô	*Rhizophora conjugata* Lam	14.7	58.3	41.7	9.6	32.0
Putut	*Bruguiera gymnorrhiza* Lam	15.5	64.3	35.7	9.0	26.7
Tumu	*Bruguiera eriopetala* W. & A.	16.1	64.0	36.0	8.8	27.2
Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	13.8	63.8	36.2	6.9	29.3

Analysis was made of some samples of mangrove bark brought from Sarawak, Borneo by Dr. Foxworthy of the botanical division of this Bureau. These barks are used by cutch factories and among the species in Borneo probably yield the highest amount of tannin.

ABSTRACTS.

Enzymatic Studies.[1] S. P. L. SORENSEN. *Comptes rendus des Travaux du Laboratoire de Carlsberg*, Vol. 8, No. 1.—1. *Acidity: Concentration of hydrogen ions.*—The rate at which molecules are split up in enzymatic reactions depends, among other things, on the acidity or alka-

[1] The paper of which this abstract embraces somewhat less than one-third, is that referred to in Procter and Jones' paper in the Feb. JOURNAL, and in Law and Sand's in the present number. The rest of the paper will appear in subsequent numbers.

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linity of the medium in which the change is going on. The degree of acidity or alkalinity in such cases is commonly calculated and reported on the basis of the total amount of base or acid added in titrating, no account being taken of the degree of dissociation of the acid or base employed, nor of the power of the solution in question to fix acids or bases.

Present-day ideas on the nature of solutions, based on the theory of electrolytic dissociation put forth by Arrhenius, ought to find application in this case. For example, when pepsic digestion takes place in N/10 hydrochloric acid, the dissociation of the HCl being incomplete, the "real" acidity, rationally called the concentration of the hydrogen ions or hydrion concentration, is a little less than the stated normality, (0.1). It is necessary, further, to take account of the salts, phosphates or others, which the solution may contain, and which may react with the hydrochloric acid, as well as other substances capable of influencing the concentration of the hydrogen ions. In the case of certain proteids which are being split up by enzymes, a part of the acid is fixed by the substance itself. Suppose two solutions one of which contains 1 gram of proteid in 100 cc. N/10 HCl and the other 5 grams of the same proteid in the same quantity of N/10 HCl. It is evident that if the proteid is one which combines with HCl, the quantity of really free acid is less in the solution containing the more proteid, although in the ordinary mode of statement both have the same acidity, since both will take the same number of cc. when titrated with N/10 NaOH. The hydrion concentration of the two solutions may be very different.

What has been said in the case of pepsic digestion in regard to degree of acidity and hydrion concentration applies to all enzymatic reactions. Pepsic digestion is chosen as a characteristic example because this reaction works better in the presence of so strong a concentration of hydrogen ions and because it is easier to observe its details, which are besides pretty well known in their main features.

Similar modes of observation may be used in the case of those enzymatic reactions which take place best in a medium which is only feebly acid, or is neutral or alkaline.

2. *Magnitude of the concentration of hydrogen ions. Index of hydrion concentration.*—Designating by C_H^+, C_{OH}^- and C_{H_2O} the concentration respectively of hydrogen ions, of hydroxyl ions and of water in an aqueous solution, we shall have by the law of mass action $\frac{C_H^+ \times C_{OH}^-}{C_{H_2O}} =$ a constant. Since in a dilute solution C_{H_2O} may be considered invariable, it follows that $C_H^+ \times C_{OH}^- =$ a constant. This constant is called the dissociation constant of water. Its commonly accepted value at 18° C. is 0.64×10^{-14}. A series of experiments made in the Carlsberg laboratory gave as a mean value 0.72×10^{-14}, or, to state

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it differently, $10^{-14.14}$. It is easily seen that this quantity permits the calculation of the hydrion concentration of an aqueous solution when the concentration of hydroxyl ions in it is known, and vice versa. A solution which has been found to be N/100 with respect to hydrogen ions is said to have a hydrion concentration of 10^{-2}, and a solution which is N/100 with respect to hydroxyl ions will have a hydrion concentration of $10^{-12.14}$, since $10^{-2} \times 10^{-12.14} = 10^{-14.14}$. By this notation, water perfectly pure, and solutions perfectly neutral, having equal numbers of hydrogen and hydroxyl ions, show a hydrion concentration of $10^{-7.07}$, ($10^{-7.07} \times 10^{-7.07} = 10^{-14.14}$). Thus the degree of concentration of the hydrogen ions is expressed as the normality of the solution in terms of hydrogen ions, a factor which is stated in the form of a negative power of 10. The numerical value of the exponent is designated by p_H^+ and is called the index, or exponent of hydrogen ions. In the examples cited above, p_H^+ has the respective values, 2, 12, 14 and 7.07.

3. *Influence of hydrion concentration compared with that of temperature*: *Curves of hydrion concentration.*—In enzymatic reactions, hydrion concentration plays a part quite analogous to that of temperature. The "curve of temperature" of an enzyme is generally understood to mean the curve obtained by taking for ordinates the quantities of matter split up in a unit of time, and for abscissas the temperatures at which the experiments have been carried out. Such a curve shows that for each enzyme there is a definite temperature, the optimum temperature, at which the splitting up takes place most rapidly.

In the neighborhood of the optimum temperature, in what may be called the optimum zone of temperature, division takes place at a speed almost equal to that observed at the optimum temperature itself. On both sides of this zone, the speed falls off, commonly most rapidly on the side toward increasing temperatures, so that if the temperature be high enough or low enough, the substance suffers very little splitting up. The sharp fall of the curve as the temperature rises above the optimum zone indicates that under these conditions the enzyme is destroyed. Thus the curve of temperatures ought to be considered as the difference of two curves, that is to say, between the "real curve of temperature," which rises as the temperature rises, and the curve of destruction of the enzyme. The latter shows very small[1] ordinates at low temperatures, as far as the optimum, and then rapidly rises with in-

[1] Such a comparison is not possible unless we adopt the same unit for the ordinates of both curves. The ordinates of the curve of destruction of the enzyme should show the difference between the quantity of matter which would be split up if the enzyme experienced no destruction, and the quantity which actually suffered molecular division under the conditions of the experiment.

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crease of temperature, quickly becoming almost parallel to the axis of ordinates.[1]

The curve of hydrogen ions of an enzyme has for ordinates the quantities of matter split up in unit time under the given experimental conditions, and for abscissas, the exponents of hydrogen ions of the liquors experimented upon.

Experiments have begun in the Carlsberg laboratory, in the attempt to determine whether the analogy which exists between the influence of temperature and that of hydrion concentration goes further, so that, for example, the drop of the two branches of the curve may be due to a milder action of the enzyme with the ionic concentrations corresponding to that branch, while the descent of the other branch is owing to an increasing destruction of the enzyme with ionic concentrations corresponding to this latter branch; or whether as is possible, the descent of both branches of the curve may be attributed to the latter cause.

In studying enzymatic reactions, it is quite as important to know the hydrion concentration with which one works, as to be aware of the other agents,—temperature for instance—which exercise an influence on the speed of the reaction.

Before explaining the methods used in measuring hydrion concentrations, the author explains why he has used in constructing the curves the exponent of the hydrion concentration, and not the hydrion concentration itself. In all enzymatic splitting up of substances, the single exception being pepsic digestion, the actual content in hydrogen ions is extremely small. For example, in the breaking up of cane-sugar by the agency of invertase an action which proceeds best in a slightly acid medium, the ionic concentration being that most favorable to the reaction, the total content of hydrogen ions in 100 cc. of the solution is less than in a single drop of N/10 HCl. In other words, if to a solution of pure cane-sugar be added invertase, freed[2] as far as possible by dialysis or other means from substances capable of fixing acids or bases, the addition of a single drop of N/10 caustic soda to 100 cc. of the solution immediately changes its character. Having been slightly acid, it becomes feebly alkaline, and the inversion entirely ceases.

For all enzymatic reactions thus far examined, the modifications of the speed with which the reaction proceeds depend, not on the absolute magnitude, but on the relative magnitude of the ionic concentration. It follows that in studies of this kind it is not convenient to calculate

[1] See for example, Th. Madsen and S. Walbum: Recherches sur l'affaiblissement de la présure (*Festskrift Tillgnad Olof Hammarsten* 1906, Afh. No. 10), and L. W. Famulener and Thorvald Madsen: Die Abschwächung der Antigene durch Erwärmung, (Bioch., *Zeitschrift*, 11, 186 (1908).

[2] It is impossible to prepare a solution of invertase completely free from substances which fix acids or bases, but on the other hand, it is not difficult to obtain an enzymatic solution sufficiently pure for the presence of minute quantities of alkali, (such, for instance, as those furnished by glass,) to make themselves distinctly felt.

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with the absolute values of the hydrion concentration, but with their logarithms, that is to say, with the before mentioned "indices of the ions." Expressed in this manner, a change in ionic concentration from 10^{-5} to 10^{-4} signifies a change equal to that produced by a modification from 10^{-2} to 10^{-1}. Also, by this method it is possible to represent graphically the influence of hydrion concentration, that is to say, by means of curves of concentration of the hydrogen ions. This would hardly be possible if the unit of abscissas were any absolute quantity of hydrogen ions, for example that corresponding to an ionic concentration of 10^{-7}. In this case, solutions having concentrations of 10^{-6} and 10^{-5} on the one hand and 10^{-8} and 10^{-9} on the other would be represented by abscissas of 10 and 100 for the first two, and 0.1 and 0.01 for the last two; and if graphic representation should embrace a still greater range of ionic concentration, the difficulties would be insurmountable.

The question arises whether these considerations of convenience correspond to a real cause: that is to say, whether the hydrion concentration enters, not with its absolute value, but with the logarithm of this value, into the equation which expresses the relation which exists between the speed of the reaction and the ionic concentration of the medium. To answer this question would necessitate a much larger number of experiments than have thus far been made.

4. *Methods of determining hydrion concentration.*—Solutions of the kind concerned in enzymatic splitting contain almost always a more or less important proportion of incompletely dissociated bodies, such as feeble acids or feeble bases, and of substances liable to be hydrolyzed, such as phosphates, or compounds which have been formed by proteids or the products of their splitting up, uniting with acids or bases. All these things are concerned in determining the content of hydrogen ions and of hydroxyl ions in the solution, and the product of these last two contents ought to be constant. If the equilibrium is disturbed, say by the introduction of a small quantity of a base, and therefore of hydroxyl ions, the re-establishment of equilibrium in the solution demands the disappearance of a certain number of hydroxyl ions. This is what takes place when, for example, the hydrolysis of the salts of feeble acids present is checked, or when the hydroxyl and hydrogen ions unite to form water, which, in its turn, results in a new formation of hydrogen ions (either by the further dissociation of weak acids, or further hydrolysis of the salts of weak bases). It is clear therefore that the addition of bases or acids to such a solution not only causes the neutralization of an equivalent portion of acid or base, but brings about at the same time phenomena of dissociation and hydrolysis, the extent of which depends on the nature and quantity of the substances which enter into play, but whose quantitative results ordinarily entirely escape estimate.

Suppose one has to do with a solution of a proteid substance in hydrochloric pepsin. In titrating by means of an appropriate indicator,

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one may estimate the proportion of acid in the solution beyond the quantity necessary to give to the mixture the hydrion concentration corresponding to the turning point of the indicator. Nevertheless, the result of the titration does not permit us to draw any conclusion in regard to the hydrion concentration of the solution titrated, for only a part of the acid titrated was in the free state; the rest has been separated little by little in the course of the titration.

The hydrion concentration ought not to be measured by any method which involves in the course of the operation a modification of that concentration, which is the case with many methods based on volumetric estimation of acidity or alkalinity.

H. Dreser[1] has pointed out a method for the estimation of free hydrochloric acid in the gastric juice which is affected by the sources of error mentioned above. After treatment of the gastric juice with solid oxalate or chromate of barium, he estimates the quantity of barium entering into solution. At the same time he determines the quantity of barium which dissolves under the same conditions when the gastric juice is replaced by hydrochloric acid diluted to so high a degree that titrated with Congo red it shows the same content of "free" hydrochloric acid as the gastric juice. From the mean of the quantities of barium found, Dreser calculates the "avidity" of the gastric juice. He himself remarks that the usual volumetric methods should not be used in the determination of hydrion concentration, not perceiving that the method which he recommends permits similar sources of error, since pure dilute hydrochloric acid is not in every respect comparable to the gastric juice. The latter contains a certain proportion of fixed hydrochloric acid, depending among other things upon the quantity of nitrogenous bodies present in the juice, and this acid may be partially liberated by shaking with the insoluble barium salt. Also, determinations made with the same liquid by means of oxalate and chromate of barium have given divergent values for the "avidity."

Another group of methods, also somewhat numerous, takes advantage of the catalytic power which the solution presents in reactions the speed of which is proportional to the concentration of hydrogen or hydroxyl ions in the medium.

The oldest of these methods is that based on the inversion of cane-sugar. This method is based on the researches of W. Ostwald,[2] and was worked out at his suggestion by F. Albin Hoffman.[3] As is well known, treatment with acids causes cane-sugar to undergo inversion, the speed of which in the case of acids sufficiently dilute, has more recently been discovered by W. Palmaer[4] to be proportional to the hydrion concentration. If now we compare the speed with which a

[1] *Beitr. zur Chem. Physiol. und Pathol.*, **8**, 285 (1906).
[2] *Journ. f. prakt. Chemie*, N. F. **29**, 385 (1884).
[3] *Centralbl. f. klin. Medicin*. **10**, 793 (1889).
[4] *Zeitschr. physik. Chemie*, **22**, 492 (1897).

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solution of cane-sugar undergoes inversion when treated with the solution to be examined, with the speed of inversion of the same sugar solution when it has been treated with a solution of hydrochloric acid of a suitable degree of dilution (whose hydrion concentration may be easily calculated), we may compute the hydrion concentration of the solution in question by a simple proportion, since the speeds of inversion are proportional to the hydrion concentrations. Since the solution examined (*e.g.* a sample of gastric juice) may sometimes contain inversive enzymes, or optically active bodies whose rotation may be modified by heat, it is necessary to take account of these possible secondary reactions by means of suitable control experiments.

Shortly afterward, F. A. Hoffman published another similar method, also based on the researches of W. Ostwald.[1] Methyl acetate, when introduced into aqueous solution, splits up into acetic acid and methyl alcohol. This reaction is accelerated by catalysis on the addition of acid, and here again the speed of saponification is proportional to the hydrion concentration. The presence of hydroxyl ions also tends to increase the speed of decomposition of ethereal salts. In the same manner by measuring the saponifying action exerted by similar solutions of ethyl acetate. J. Shields[2] has estimated the content of hydroxyl ions in the solutions of salts of feeble acids.

Another method of the same kind is that pointed out by K. Koelichen[3] for measuring the concentration of hydroxyl ions. This author has shown that the transformation of diacetonyl alcohol into acetone:

$$CH_3.CO.CH_2C(OH)(CH_3)_2 = 2CH_3.CO.CH_3$$

takes place spontaneously and with a considerable increase of volume, so that it may be measured by the amount of expansion. The splitting up is favored by the presence of hydroxyl ions, and the speeds are proportional to the concentration of these ions.

Finally, G. Bredig and W. Fraenkel[4] have recently worked out a beautiful method for the determination of hydrion concentration by using as the basis of their process the splitting up, described by Th. Curtius,[5] of diazoacetic ether in the presence of a dilute acid, with the evolution of free nitrogen:

$$N_2.CH.COOC_2H_5 + H_2O = N_2 + CH_2OH.COOC_2H_5.$$

The quantity of nitrogen released is easily measured, and the reac-

[1] W. Ostwald, *Journ. f prakt. Chemie*, N. F. **28**, 449 (1883). J. Walker, *Zeitschr. physik. Chemie*, **4**, 322 (1899); F. A. Hoffman, Verh. des X intern. medic. Congresses, Berlin, 1890, Abth. V. p. 201.

[2] *Zeitschr. physik. Chemie*, **12**, 167 (1893).

[3] *Ibid.*, **33**, 129 (1900); compare also W. Will and G. Bredig: Umwandlung von Hyoscyamin in Atropin durch Basen. Ber. der deutschen chem. Ges. **21**, 2777 (1888).

[4] *Zeitschr. f. Electrochemie*, **11**, 525 (1905); *Zeitschr. physik. Chemie*, **60**, 202 (1907); compare also Bror. Holmberg, *Ibid.*, **62**, 726 (1908).

[5] *Jour. f. prakt. Chemie*, N. F., **38**, 396 (1888).

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tion is purely monomolecular. The speed of the reaction is proportional to the hydrion concentration and the catalytic action is considerable, so that quite feeble concentrations can be measured.

In the case of the methyl acetate method, the increase of hydrion concentration due to the acetic acid formed in the reaction is of very little importance, since that acid dissociates but little. The methods which have been described are not on the whole very satisfactory, because they do not work well except in the case of relatively strong concentrations, which practically limits them to a single case of enzymatic reaction, that of pepsic digestion.

The measurement of hydrion concentration ought to be made at a temperature as near as possible to that which it is proposed to employ in the enzymatic reaction itself which is to be investigated.

In the application of any of these methods, as for example the inversion of cane-sugar by acetate of methyl or diacetonyl alcohol, it is necessary to take account of what is conveniently called "the effect of neutral salts,"[1] as well as of the fact not less important that even if the method is applied easily to solutions of simple composition, it may sometimes be entirely inapplicable in the case of highly complex mixtures such as are generally involved in enzymatic reactions. G. Bredig and P. F. Ripley[2] have shown that the diazoacetic ether method fails if the medium contains even the slightest trace of chlorine or SO_4 ions, for in this case accessory reactions occur at the same time that the hydrion concentration undergoes a modification. For example,

$$N_2CH.COOC_2H_5 + HCl = N_2 + CH_2Cl.COOC_2H_5.$$

In attempting to determine the content of hydroxyl ions in the blood by the diacetonyl alcohol method described by Koelichen, Taav. Laitinen[3] has obtained a value whose order of magnitude is quite different from that ordinarily found.

The second group of methods are not of general application, and if one of them should be employed in a particular case, it should be rigorously checked.

Two other methods are known by which the concentration of hydrogen or hydroxyl ions in a solution may be determined. These are the measurement by means of the gas electrode and the method of indicators, called also respectively, the electrometric and colorimetric methods.

These are the two methods which have been used in the enzymatic researches at the Carlsberg laboratory. They supplement each other. The electrometric is the more exact, but is much more complicated, while the colorimetric method, although less precise, is very simple in execution. The author has recognized the need of a simple method of

[1] Arrhenius, *Zeitschr. physik. Chemie*, 1, 110 (1887); 4, 237 (1889); 31, 197.

[2] *Berichte d. d. chem. Ges.*, 40, 4015 (1907); see also W. Fraenkel: *Zeitschr. physik. Chemie*, 60, 202 (1907).

[3] *Festskrift tillegnad Olof Hammarsten*, 1906, Afh. Nò. IX.

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determining hydrion concentration, and has made extensive researches in regard to the applicability of various indicators. The electrometric method has also been employed, and a comparison of the two has been made.

Electrometric Method.—When a platinum plate covered with platinum black is placed in an aqueous solution acid, neutral, or alkaline, and when this plate is saturated with hydrogen, there will be a difference of potential between the solution and the immersed platinum, the magnitude of the difference depending on the hydrion concentration of the solution. The hydrion concentration may therefore be determined by measuring this difference of potential.[1]

Colorimetric Method.—The end point of a titration shows that the hydrion concentration of the solution tested has or has not reached, or has even passed, a certain intensity, different for the different indicators, and which shows the ionic concentration at the turning point of the indicator considered. Thus by the color which a solution takes when an indicator is added, one can decide whether this solution has a hydrion concentration higher or lower than that which corresponds to the turning point of the indicator.

It is this simple principle which forms the basis of the method of indicators, or the colorimetric method. The principle has been known a long time, but it was not until the remarkable researches of Friedenthal and Salm[2] that the scattered materials were examined and in part completed, so that they have established a complete series of indicators presenting turning points at the most diverse hydrion concentrations. It is therefore to these two scientists that the honor is due for working out the first colorimetric method for the determination of hydrion concentration. Their results, however, are not applicable to enzymatic research without additional investigation, since a method which works with comparatively simple substances may fail when tried with the very complex substances which so often take part in enzymatic reactions. It is necessary to investigate the applicability of each indicator to the case of each solution. A hundred different indicators have thus been examined, the work covering a period of several years. Publication was long postponed in order to test the value of the method.

If something more than a purely qualitative appreciation is needed it will be possible to judge of the intensity on the shade of a color only by comparing it with similar intensities or shades. The task which first presented itself was to prepare solutions suitable to serve as standards, which mixed together in convenient proportions, permit

[1] W. Nernst, *Zeitschr. physik. Chemie*, 4, 129 (1889).

[2] H. Friedenthal, *Zeitschrift für Electrochemie*, 10, 113 (1904: Ed. Salm, *Ibid.*, 10, 341 (1904); 12, 99 (1906); Ed. Salm and H. Friedenthal, *Ibid.*, 13, 125 (1907); Ed. Salm, *Zeitschr. physik. Chemie*, 57, 471 (1906), 63, 83 (1908); compare also W. Salesky, *Zeitschr. f. Electrochemie*, 10, 204, (1904), and Bruno Fels, *Ibid.*, 10, 208 (1904).

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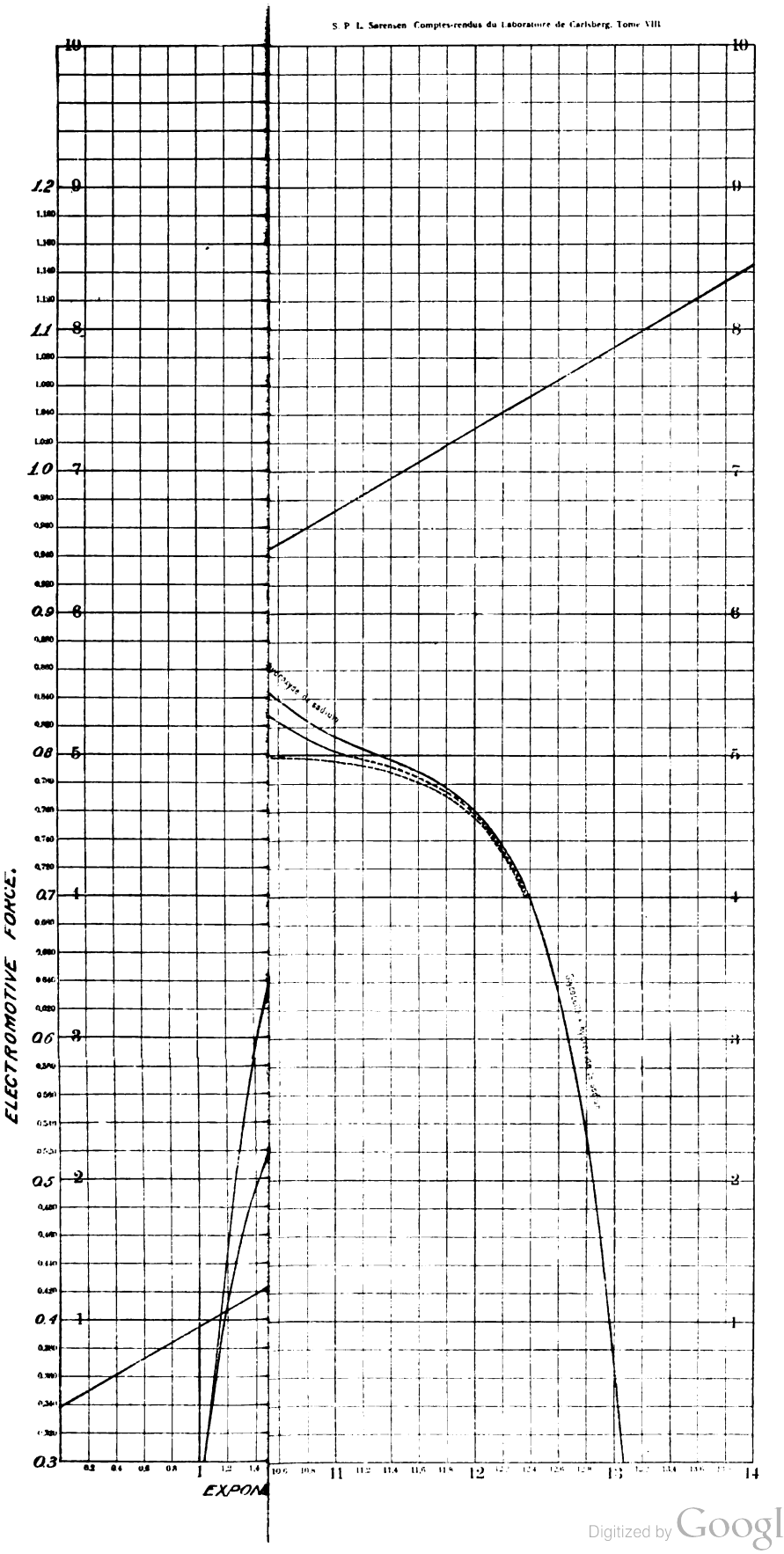

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one to obtain liquors for comparison possessing hydrion concentrations established exactly in advance in each particular case. It was necessary that these standard solutions should be easy to prepare, and moreover, that they should present a constitution such that the liquors of comparison obtained from them should always have (practically speaking) the same hydrion concentration, even if the standard solutions had stood months at a time, for example in a glass flask of alkaline reaction. In this process were used a number of simple substances guaranteed pure, furnished by C. A. F. Kahlbaum, in Berlin. After dissolving them in boiled water, they are preserved in Woulff bottles provided with a burette and the usual arrangement which allows the liquor to be taken out without admitting carbonic acid from the air. By mixing these liquids in convenient proportions, liquors of comparison may be procured possessing a hydrion concentration of from about 10^{-1} to 10^{-13}.

Next comes the question of which indicators are most suitable, which presents much greater difficulties. Most indicators in fact are apt to combine with natural proteid substances, and there are some which unite even with the products of more or less advanced decomposition of proteids. As a result, even if the combinations are not always indicated by a visible deposit, the indicator does not change color at all in most cases and hence becomes useless. This is the reason, as has been said, that it was necessary to prove the excellence of each particular indicator, and to determine the degree of precision which it will give.

For this it was necessary to prepare a large number of different mixtures, principally of proteid substances and of their products of decomposition. The real hydrion concentration of these mixtures had been determined by an electrometric measure which thus served as a fundamental method. There are some indicators (*e. g.*, *p.* nitrophenol and phenolphthalein) which possess a very extensive usefulness, while there are also some which are found entirely useless after the products of the splitting of proteids even rather well demolished come into play. Congo red, used so much in physiology, comes under the latter category.

We have already noted above that in enzymatic reactions where neither the material nor its products of decomposition are capable of fixing acids on bases (*e. g.* in the inversion of cane-sugar by invertase) it may often be difficult to keep the hydrion concentration constant because the alkaline ingredients coming from the glass, or in other cases the carbonic acid of the air may exercise a marked influence. In this case it is suitable to fix the amount of ionic concentration by adding a buffer ("tampon"). We mean by this a suitable mixture of salts which have no appreciable influence on the speed of the enzymatic reaction, but which keep the hydrion concentration constant in the course of the experiment. In order to do this it is necessary that the buffer be so constituted that a contribu-

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tion of small portions of acid or base cannot sensibly influence the hydrion concentration. Nature herself makes use of such buffers consisting ordinarily of a mixture of phosphates sometimes also of a mixture of carbonates or even of proteids and their products of decomposition. The mixtures of standard solutions mentioned above and used in the colorimetric method, make good buffers.

As has been indicated above, there is no doubt that the question of hydrion concentration extends beyond the limits of enzymology, properly speaking. The amount of ionic concentration is certainly an element which must be reckoned with all the processes of biology.

Granting that in this study it may often be important to keep the experimental conditions including the hydrion concentration as constant as possible, it will not be difficult to cite cases where the addition of an appropriate buffer might be very useful. The liquors used as nourishing mediums for microörganisms are an example. The growth of the organisms often causes a modification of the hydrion concentration of the medium, unless the latter contains a sufficient quantity of substances capable of fixing acids or bases, that is, a suitable buffer.

A. *Electrometric Measurements.—a.* Methods of measurement. For all the measurements of this kind a similar experimental arrangement was used. The cell whose electromotive force was measured consisted of one calomel electrode plunged in a N/10 solution of chloride of potassium and one hydrogen electrode (a platinum plate coated with platinum black) immersed in the solution to be examined which served as an electrolytic liquor. The potential of diffusion between the two solutions was eliminated by the method indicated by N. Bjerrum[1] to wit, the interposition between the two electrolytic solutions of either a 3.5 normal solution of chloride of potash or a 1.75 normal solution of the same salt after which the correction was made by the addition of the difference between the two potentials found.

R. Abegg and A. C. Cumming[2] have proposed to replace the chloride of potassium by ammonium nitrate, whose ions have likewise practically the same speed of displacement, but whose solubility in water is much greater than that of chloride of potash. Without doubt a strong solution of ammonium nitrate could ordinarily be used for the examination of acid liquors, and it would allow the potential of diffusion to be completely eliminated, and thus avoid the correction which is in any case more or less uncertain. The nitrate, however, cannot be used with alkaline liquids, and the Bjerrum process has the advantage of being applicable to either acid or alkaline liquids.

The apparatus used was of exactly the same kind as that described in the work of N. Bjerrum quoted above. In general the operative process indicated by N. Bjerrum was followed.

Coated platinum as well as calomel electrodes were prepared exactly in the manner indicated in the "Physiko-chemische Messungen" by

[1] *Zeitschr. physik. Chemie*, 53, 428 (1905).

[2] *Zeitschr. für Electrochemie*, 13, 17 (1907).

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Ostwald-Luther (1902). The measurements were taken according to the compensation method of Poggendorff, by the aid of a Lippmann electrometer furnished with an oval capillary, and large enough to be used to zero. The measuring wire which was a meter long and was divided into millimeters, was carefully corrected by means of measurements made in the physical laboratory of the Carlsberg polytechnical school by Mr. Thorkelsson and Mr. Hansen. The normal element used was a Weston cell whose electromotive force at 18° C. was 1.0191 volts.

The hydrogen used was prepared from a 10 per cent. solution of potash by the aid of iron electrodes. After having washed the hydrogen first twice with an alkaline solution of pyrogallol, then in pure water, it was passed through a cylindrical glass containing pure cotton, from whence it was introduced into the vessel enclosing the electrode, after having been washed with a little of the solution to be examined.

The measurements were made in a room whose temperature was kept as nearly as possible at 18° C., the normal temperature of all the experiments (it rarely deviated half a degree). The barometric reading underwent great changes (from 722 to 794 mm.) during the long space of time which these experiments lasted, and consequently all the measurements have been reduced to a pressure of 760 mm.

b. Determination of π_o.

Let us designate by π_p the electromotive force of a cell composed of one calomel electrode plunged in a N/10 solution of chloride of potassium and an electrode of hydrogenized platinum placed in an electrolytic liquor whose hydrion concentration expressed with a normal hydrion solution as unity is C_p $(= 10^{-p})$. If then we designate by π_q and C_q $(= 10^{-q})$ the corresponding quantities of a similar cell, we shall have

$$\pi_p - \pi_q = K \log \frac{C_q}{C_p}. \qquad (I)$$

where K may be supposed, with a sufficient approximation, equal to $0.0577 + 0.0002\ (t° - 18°)$.[2]

If by experiment, we determine π_p for an electrolytic liquid, say hydrochloric acid conveniently dilute, whose hydrion concentration C_p may be calculated by means of the normality of the acid (A_p) and its degree of dissociation (α); and if in equation (I) above, the values of π_p and C_p are substituted, this equation will contain no other unknowns but π_q and C_q, so that π_q may be calculated for some value of C_q and *vice versa*. In designating by π_o the electromotive force of a cell of the kind used here, and where

[1] W. Ostwald, Lehrbuch der Allgemeinen Chemie, Zweite Aufl. Band 2, Teil 1, p. 895 (1893); F. I. Small, *Zeitschr. physik. Chemie*, 14, 582 (1894).

[2] W. Nernst, *Zeitschr. physik. Chemie.*, 4, 129 (1889); *Zeitschr. f. Elektrochemie*, 10, 630 (1904).

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the electrolytic liquid surrounding the hydrogen electrode is normal with respect to the hydrogen ions ($C_o\ 10^{-o} = 1$) we shall have

$$\pi_o = \pi_p - 0.0577 \log \frac{C_o}{C_p} = \pi_p - 0.0577 \log \frac{1}{C_p}. \qquad (II)$$

In table 1 which follows are collected a considerable number of measurements made by means of hydrochloric acid of different concentrations, for the purpose of determining the value of π_o.

The first column of the table represents the composition of the solutions examined, while the concentration of the hydrochloric acid varies greatly (from N/10 to N/200) the concentration of the total chlorine is kept constant, viz., equal to N/10 with the exception of one experiment. Following Arrhenius[1] a like degree of dissociation (a) of the hydrochloric acid is assumed in all the solutions. Assuming the figure found by Kohlrausch[2] for the molecular conductivity of N/10 hydrochloric acid at 18° C. (351) and supposing the molecular conductivity at an infinite dilution equal to 383 and we shall have $a = 0.9165$. In the exceptional experiment on N/100 hydrochloric acid without the addition of sodium chloride we shall have $a = 0.9661$.

In the second column is the hydrion concentration of the solution (C.) a figure obtained simply by multiplying the degree of dissociation by the normality of the acid. The third column gives the value of the product $0.0577 \times \log \frac{1}{C}$.

In the fourth and fifth columns of the table are entered the electromotive forces with the substitution respectively of 1.75 normal and 3.5 normal solutions of chloride of potash, and the sixth column contains the value of π corrected by means of these two values. Finally the last column contains the value of π_o calculated by means of equation (II) indicated above.

It is indicated in the table by transverse spaces that the measurements may be arranged in four series of experiments, the first of which was executed some three years ago by the author, while the three others were made at different times by Mr. S. Palitzsch.

The mean value of π_o taken from all the measurements is 0.3377, and the deviation from this mean is in only one case greater than one millivolt; generally it is much less. The differences between these experiments are of the same order of magnitude as those in the measurements made by N. Bjerrum,[3] but the mean here given (0.3377) is higher by one millivolt than that found by Bjerrum (0.3367), and moreover it agrees excellently with that found by Bjerrum in his experi-

[1] *Zeitschr. physik. Chemie.*, 31, 204 (1899).

[2] F. Kohlrausch and L. Holborn, *Das Leit vermögen der Elektrolyte*, 1898, p. 160.

[3] See *Zeitschr. physik. Chemie*, 53, 432 (1905). Mém. de l'Acad. Roy. de Danemark. [7], Sect. d. Sc. t., IV, 15. Studier over basiske Kromiforbindelser, p. 38 (1908).

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TABLE I.—Electromotive Force π_0 of a Cell Composed of One Calomel Electrode Plunged into a N/10 Solution of Chloride of Potash, and One Hydrogenized Platinum Electrode Placed in a Solution Normal with Respect to Hydrogen Ions at 18° C.

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times \alpha)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π corrected	$\pi_0 = \pi(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4066	0.4020	0.3974	0.3375
0.1 n	0.0916_5	0.0599	0.4082	0.4029	0.3976	0.3377
0.05 n + NaCl 0.5 n.....	0.0458_3	0.0773	0.4219	0.4184	0.4149	0.3376
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4415	0.4401	0.43°7	0.3385
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4569	0.4560	0.4551	0.3375
0.005 n + NaCl 0.095 n.....	0.00458_3	0.1350	0.4733	0.4733	0.4733	0.3383
0.01 n (without NaCl).....	0.00966_1	0.1163	0.4599	0.4571	0.4543	0.3380
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4402	0.4392	0.4382	0.3380
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4390	0.4382	0.4374	0.3372
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4576	0.4568	0.4560	0.3384
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4569	0.4563	0.4557	0.3381
0.005 n + NaCl 0.095 n.....	0.00458_3	0.1350	0.4733	0.4733	0.4733	0.3383
0.005 n + NaCl 0.95 n.....	0.00458_3	0.1350	0.4726	0.4726	0.4726	0.3376

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TABLE I.—ELECTROMOTIVE FORCE π_o OF A CELL COMPOSED OF ONE CALOMEL ELECTRODE PLUNGED INTO A N/10 SOLUTION OF CHLORIDE OF POTASH, AND ONE HYDROGENIZED PLATINUM ELECTRODE PLACED IN A SOLUTION NORMAL WITH RESPECT TO HYDROGEN IONS AT 18° C.—(*Continued*).

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times \alpha)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π_o corrected	$\pi_o = \pi(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4070	0.4022	0.3974	0.3375
0.1 n	0.0916_5	0.0599	0.4064	0.4015	0.3966	0.3367
0.1 n	0.0916_5	0.0599	0.4065	0.4017	0.3969	0.3370
0.1 n	0.0916_5	0.0599	0.4063	0.4015	0.3967	0.3368
0.06 n + NaCl 0.04 n	0.0549_9	0.0727	0.4167	0.4134	0.4101	0.3374
0.06 n + NaCl 0.04 n	0.0549_9	0.0727	0.4170	0.4134	0.4098	0.3371
0.04 n + NaCl 0.06 n	0.0366_6	0.0828	0.4252	0.4227	0.4202	0.3374
0.04 n + NaCl 0.06 n	0.0366_6	0.0828	0.4251	0.4225	0.4199	0.3371
0.02 n + NaCl 0.08 n	0.0183_3	0.1002	0.4405	0.4390	0.4375	0.3373
0.02 n + NaCl 0.08 n	0.0183_3	0.1002	0.4404	0.4389	0.4374	0.3372
0.01 n + NaCl 0.09 n	0.00916_5	0.1176	0.4566	0.4555	0.4544	0.3368
0.01 n + NaCl 0.09 n	0.00916_5	0.1176	0.4560	0.4553	0.4546	0.3370

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TABLE I.—Electromotive Force π_0 of a Cell Composed of One Calomel Electrode Plunged into a N/10 Solution of Chloride of Potash, and One Hydrogenized Platinum Electrode Placed in a Solution Normal with Respect to Hydrogen Ions at 18° C.—(*Continued*).

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times \alpha)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π corrected	$= \pi_0(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4082	0.4032	0.3982	0.3383
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4187	0.4148	0.4109	0.3382
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4187	0.4146	0.4105	0.3378
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4267	0.4241	0.4215	0.3387
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4273	0.4243	0.4213	0.3385
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4418	0.4402	0.4386	0.3384
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4419	0.4403	0.4387	0.3385
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4420	0.4406	0.4392	0.3390
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4410	0.4393	0.4376	0.3374
					Mean,	0.3377

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ments using Planck's formula for the elimination of the potential of diffusion.

If the hydrogen electrode is as it should be, it is easy in measuring solutions such as those under discussion, to obtain constant results. Measurements of the same solution usually differ by only a few tenths of a millivolt. Slightly greater variations occur in the table, and the factors which might influence the exactness of the result are next discussed.

The solutions examined had all been prepared with such care that they presented no differences of composition electrically measurable. Ordinarily more than one calomel electrode was used, and in the rare cases where one electrode gave results differing by more than two or three-tenths of a millivolt from the values obtained (in otherwise similar conditions) from the other calomel electrodes, the defective electrode was thrown away. Thus there was slight probability of errors.

With the hydrogen electrodes the case is not the same. Two hydrogen electrodes do not always act exactly alike, and it may even happen, although rarely, that a perfect electrode may suddenly give false results. It is therefore necessary to pay continual attention to the hydrogen electrodes, and to take care to verify their normality. As a control we measured at intervals some mixtures taken from the solutions described below, for example, a mixture composed of eight volumes of the solution of glycocoll and two volumes of N/10 hydrochloric acid. These mixtures were chosen so that their composition excluded the possibility that a slight impurity, perhaps from alkaline ingredients coming from the glass might influence the result of measurement. Mixtures were chosen for which no corrections were necessary, in order to avoid possible errors due to inaccurate corrections. An effective control is thus obtained, so that electrodes of abnormal action may be rejected. On the whole, the probable limit of error is perhaps less than ½ a millivolt.

The method of eliminating the potential of diffusion by means of a correction also introduces a source of error which must be taken into account. On the other hand the table does not show the least indication of a relation between the size of the correction and the value of π_o. It is proved that the magnitude of the correction diminishes nearly proportionately to the hydrion concentration in solutions in which one may consider the concentration of chlorine ions as constant.

Composition of solutions	0.1 N. HCl	0.06 N. HCl 0.04 N. NaCl	0.05 N. HCl 0.05 N. NaCl	0.04 N. HCl 0.06 N. NaCl	0.02 N. HCl 0.08 N. NaCl	0.01 N. HCl 0.09 N. NaCl	0.005 N. HCl 0.095 N. NaCl
Mean value of the correction in millivolts..	4.9	3.7	3.5	2.7	1.4	0.8	0.0

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Thus there is scarcely room to believe that the correction can have had the effect of disturbing in one way or the other the mean of the mean values of π_o. In considering how the corrections for the undividual experiments differ from the mean values of the correction indicated above, it will be seen that the error connected with a determination as a result of the correction could not be calculated to less than half a millivolt.

In measurements of this kind it is necessary to insulate as completely as possible all the articles used. In the course of these experiments certain difficulties were encountered due without doubt to defective insulation, and they were only conquered by placing, by the advice of Professor Prytz, each piece of measuring apparatus on a block of paraffine on the one hand, and then by passing the hydrogen through two tubes containing chloride of calcium and connected by a glass tube, in its passage from the electrolytic gas generating apparatus the vessel enclosing the electrode. This arrangement prevented the formation on the inside of the latter tube of a layer of moisture conducting electricity. Formerly it sometimes happened that when the short circuit ceased or a new one was introduced the capillary electrometer showed the existence of a difference of tension more or less strong, even when the electrometer was not connected in any circuit. With these precautionary measures no measurable movement of the mercury column was observed when the circuit was broken.

Substituting the value of π_o in equation (II), we have:

$$\pi_p = 0.3377 + 0.0577 \log \frac{1}{C_p}. \qquad \text{(III)}$$

In all the cases discussed here C_p (which means the normality of the solution with respect to hydrogen ions, or in other words the number of gram-ions of hydrogen per liter) is smaller than 1 and can be placed equal to 10^{-p}, where for the number p, the author proposes the name "index of hydrogen ions" and the designation of p_H^+. The index of hydrogen ions $\left(p_H^+\right)$ of a solution means therefore the logarithm of the reciprocal of the normality of the solution relative to the hydrogen ions.[1]

By introducing in formula (III) above the value $10^{-p_H^+}$ for C_p, we shall have

$$\pi = 0.3377 + 0.0577 \times p_H^+. \qquad \text{(IV)}$$

$$p_H^+ = \frac{\pi - 0.3377}{0.0577}. \qquad \text{(V)}$$

[1] As it is not usual to have solutions stronger than normal with respect to hydrogen ions, the above definition of the index of hydrogen ions has been chosen, which therefore will generally be a positive number. It will only be negative when the solution is stronger than normal.

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It will be seen that by means of these last two equations one can calculate π when the hydrion concentration is given and thus the index of hydrogen ions and *vice versa*. Besides it is clear that the relation between π and p_H^+ may be expressed graphically by a straight line, which, when the values of π are ordinates and those of p_H^+ abcissas, will cut the axis of ordinates at the point 0.3377 and whose direction is entirely determined by the factor 0.0577. By changing the value π_o (0.3377) this line would be displaced in the system of coördinates, but the direction would not change. On the contrary the latter will vary with temperature, seeing that the factor 0.0577 is valid only at 18° C.

On the main chart of curves will be found this "line" designated as the *line of exponents*. The significance of this line is that by means of it we can, without any calculation graphically convert a value measured in π into the corresponding value of p_H^+, and inversely.

C. DETERMINATION OF THE DISSOCIATION CONSTANT OF WATER.

As has already been said in the introduction, it is usually easiest to calculate with the hydrion concentration because it is more susceptible of direct and exact determination than is the concentration of hydroxyl ions. There are many cases where it is easier to determine the hydroxyl ion content of an alkaline liquid; it therefore becomes very important to know exactly the constant of dissociation of water, a quantity which has very often been determined in entirely different ways, with results fairly concordant. A new determination of this has been made by the aid of the gas electrode.

The principle of the process is as follows:—by electrometric measurements by the method described above the hydrion concentration was determined in some solutions conveniently diluted with sodium hydroxide. The degree of dissociation of these solutions was known and consequently also the hydroxyl ion concentration. By multiplying the measured hydrion concentration by the calculated hydroxyl ion concentration the constant of dissociation of water was determined.

A test was made to determine whether the correction (which was of different magnitude in solutions of different concentrations) introduced a source of noticeable error. It appears from what follows that it does not, and this result indicates that even in the case of liquids rather strongly alkaline, it is safe to use the method of correction proposed by Bjerrum. The experiments in question are recorded in Table 2.

In the first column of this table is indicated the composition of the solutions examined. It appears that the concentration of the sodium hydroxide underwent great variations (from N/10 to N/100) while the whole content of sodium was the same (N/10) in all the experiments. For this reason the calculations are made for the same degree of dissociation (α) for the sodium hydroxide in all the experiments.

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TABLE II.—Dissociation Constant of Water at 18° C.

Composition of solutions	Concentration of hydroxyl ions	π, 1.75 normal solution KCl	π, 3.5 normal solution KCl	π corrected	Hydrion concentration calculated from mean of π corrected $\left(C_H^+ = 10^{-p}\right)$	Constant of dissociation of water	
						$10^{-(p+q)}$	$k \times 10^{-14}$
	q				p	$p+q$	k
0.1 n NaOH	1.075	1.0849	1.0871	1.0893	13.026	14.101	0.793
0.1 n NaOH	1.075	1.0861	1.0880	1.0899	13.036	14.111	0.774
0.1 n NaOH	1.075	1.0873	1.0892	1.0911	13.057	14.132	0.738
0.1 n NaOH	1.075	1.0876	1.0895	1.0914	13.062	14.137	0.729
0.1 n NaOH	1.075	1.0852	1.0871	1.0890	13.021	14.096	0.802
0.1 n NaOH	1.075	1.0848	1.0867	1.0886	13.014	14.089	0.815
0.05 n NaOH + 0.05 n NaCl	1.376	1.0700	1.0713	1.0726	12.736	14.112	0.773
0.05 n NaOH + 0.05 n NaCl	1.376	1.0699	1.0708	1.0717	12.721	14.097	0.800
0.02 n NaOH + 0.08 n NaCl	1.775	1.0480	1.0488	1.0496	12.338	14.113	0.771
0.02 n NaOH + 0.08 n NaCl	1.775	1.0478	1.0487	1.0496	12.338	14.113	0.771
0.01 n NaOH + 0.09 n NaCl	2.075	1.0315	1.0315	1.0315	12.024	14.099	0.796
0.01 n NaOH + 0.09 n NaCl	2.075	1.0316	1.0316	1.0316	12.026	14.101	0.793
0.01 n NaOH	1.075	1.0890	1.0910	1.0930	13.090	14.165	0.684
0.01 n NaOH	1.075	1.0885	1.0902	1.0919	13.071	14.146	0.715
0.01 n NaOH	1.075	1.0884	1.0900	1.0916	13.066	14.141	0.723
0.06 n NaOH + 0.04 n NaCl	1.297	1.0767	1.0780	1.0793	12.853	14.150	0.708
0.06 n NaOH + 0.04 n NaCl	1.297	1.0772	1.0786	1.0800	12.865	14.162	0.689
0.04 n NaOH + 0.06 n NaCl	1.474	1.0673	1.0683	1.0693	12.679	14.153	0.703

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TABLE II.—DISSOCIATION CONSTANT OF WATER AT 18° C.—(*Continued*).

Compositions of solutions	Concentration of hydroxyl ions	π, 1.75 normal solutions KCl	π, 3.5 normal solution KCl	π corrected	Hydrion concentration calculated from mean of π corrected	Constant of dissociation of water	
					$\left(C_{\frac{+}{H}}=10^{-p}\right)$	$10^{-(p+q)}$	$k\times10^{-14}$
	q				p	$p+q$	k
0.04 n NaOH + 0.06 n NaCl.....	1.474	1.0675	1.0685	1.0695	12.683	14.157	0.697
0.02 n NaOH + 0.08 n NaCl.....	1.775	1.0509	1.0514	1.0519	12.378	14.153	0.703
0.02 n NaOH + 0.08 n NaCl.....	1.775	1.0508	1.0514	1.0520	12.379	14.154	0.701
0.01 n NaOH + 0.09 n NaCl.....	2.075	1.0345	1.0345	1.0345	12.076	14.151	0.706
0.01 n NaOH + 0.09 n NaCl.....	2.075	1.0343	1.0343	1.0343	12.073	14.148	0.711
0.1 n NaOH	1.075	1.0887	1.0902	1.0917	13.067	14.142	0.721
0.1 n NaOH	1.075	1.0880	1.0901	1.0922	13.076	14.151	0.706
0.1 n NaOH	1.075	1.0873	1.0889	1.0905	13.047	14.122	0.755
0.1 n NaOH	1.075	1.0872	1.0895	1.0918	13.069	14.144	0.718
0.1 n NaOH	1.075	1.0877	1.0902	1.0927	13.085	14.160	0.692
0.06 n NaOH + 0.04 n NaCl.....	1.297	1.0759	1.0771	1.0783	12.835	14.132	0.738
0.06 n NaOH + 0.04 n NaCl.....	1.297	1.0763	1.0778	1.0793	12.853	14.150	0.708
0.06 n NaOH + 0.04 n NaCl.....	1.297	1.0762	1.0778	1.0794	12.854	14.151	0.706
0.04 n NaOH + 0.06 n NaCl.....	1.475	1.0668	1.0679	1.0690	12.674	14.148	0.711
0.04 n NaOH + 0.06 n NaCl.....	1.475	1.0673	1.0683	1.0693	12.679	14.153	0.703
0.02 n NaOH + 0.08 n NaCl.....	1.775	1.0507	1.0512	1.0517	12.374	14.149	0.710
0.02 n NaOH + 0.08 n NaCl.....	1.775	1.0507	1.0514	1.0521	12.381	14.156	0.698

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Accepting the figures of Kohlrausch[1] for the molecular conductivity of a N/10 solution of sodium hydroxide (183), and making the molecular conductivity at an infinite dilution equal to 217.6 (the sum of the speeds of displacement of the two ions 43.6 + 174.[2] We shall have $a = 0.841$.

In the second column is found the concentration of hydroxyl ions calculated by means of the degree of dissociation and the content of sodium hydroxide. The third and fourth columns indicate the electromotive force measured by interposing one after the other two solutions 1.75 normal and 3.5 normal, of chloride of potassium. The fifth column contains the value of π corrected according to equation V above.

The last two columns give the product of the hydrion and hydroxyl ion concentrations of the measured solutions, the product expressed either by a negative fractional power of 10 or by a factor multiplied by 10^{-14}.

The transverse spaces indicate that the measurements were made in three series at different times on different materials, and each time with freshly prepared solutions. The value of the constant of dissociation of water has been found higher in the first series than in the two others, the mean of k in the three series of experiments being 0.78_6, 0.70_4 and 0.71_4. The first series was done before, the other two after the adoption of the precautionary measures mentioned above, so that it is reasonable to have more confidence in the values found latest. In the calculation of the total mean double importance has been given to the values of the second and third series. The mean value, calculated in this way, of the dissociation constant of water at 18° is

$$0.72 \times 10^{-14} = 10^{-14.14}.$$

Consequently, in pure water and in really neutral solutions the concentration of hydrogen and of hydroxyl ions will be $0.85 \times 10^{-7} = 10^{-7.07}$.

It will be observed that the variations from the mean are greater in Table 2 than in Table 1, sometimes exceeding 2 millivolts. Under normal conditions such errors rarely occur.

It appears from Table 2 that the correction does not introduce an appreciable error, for the constant k in the last column does not vary with the correction. As will appear from the small table below, the correction diminishes with the concentration of the sodium hydroxide.

Composition of solutions	0.1 Normal NaOH	0.06 N. NaOH 0.04 N. NaCl	0.05 N. NaOH 0.05 N. NaCl	0.04 N. NaOH 0.06 N. NaCl	0.02 N. NaOH 0.08 N. NaCl	0.01 N. NaOH 0.09 N. NaCl
Mean value of the correction in millivolts..	1.9	1.4	1.1	1.0	0.7	0.0

[1] F. Kohlrausch and L. Holborn, *Das Leit vermögen der Elektrolyte*, 1898, p. 160.

[2] F. Kohlrausch, *Lehrbuch der praktischen Physik*, (1901) p. 596.

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For comparison, the more important determinations of the constant of dissociation of water are here briefly described. The coefficient of temperature is so great that in order to reduce to 18° C. the values obtained at 25° C., it is necessary to subtract about 24 per cent.[1]

First. By means of the gaseous chain between normal acid and normal base, W. Ostwald[2] found a difference of potential of about 0.7 volt, from which W. Nernst[3] deduces the constant of dissociation of water at 18° C $= 0.64 \times 10^{-14}$.

Second. From the experiments of Shield on the hydrolysis of sodium acetate, S. Arrhenius[4] derives the value 1.27×10^{-14} for 25°. Reduced to 18° this gives 0.73×10^{-14}.

Third. At the suggestion of van't Hoff, J. J. A. Wijs[5] has observed the speed of saponification of methyl acetate in pure water, and gets the value 1.44×10^{-14}, at 24.8° C., or 0.83×10^{-14} at 18° C.

Fourth. In determining the conductivity of water purified with every possible care, F. Kohlrausch and Ad. Heydweiller[6] have found that 1 liter of water contains at 18° C., $0.8 \times$ —[7] grams of hydrogen ions, and at 25° C., 1.05×10^{-7} gram. From this the constant of dissociation of water is calculated as follows:

$$\left(\frac{0.8}{1.008} \times 10^{-7}\right)^2 = 0.63 \times 10^{-14} \text{ at } 18°$$

and

$$\left(\frac{1.05}{1.008} \times 10^{-7}\right)^2 = 1.09 \times 10^{-14} \text{ at } 25°.$$

Fifth. At 25° to 26° C., R. Lowenherz[7] has measured the electromotive force of a cell composed of two hydrogen electrodes, one immersed in N/10 or N/100 hydrochloric acid, and the other in N/10 or N/100 sodium hydroxide. The intermediate liquid was an equimolecular solution of lithium chloride, and the potentials of diffusion were calculated according to Planck. The principle of this method was therefore exactly the same as that which forms the basis of Sorensen's experiments. Eight experiments[8] on N/10 hydrochloric acid and N/10 sodium hydroxide gave Lowenherz 1.187×10^{-7} and six experiments[9] with the same substances in N/100 solution gave 1.075×10^{-7}. The mean of these two values gives for the constant of dissociation of water at 25° to 26° C., 1.28×10^{-14}, or about 0.74×10^{-14} at 18° C.

[1] Kohlrausch and Heydweiller, *Wied. Ann.*, 53, 234 (1894).

[2] *Zeitschr. physik. Chemie*, 11, 521 (1893).

[3] *Zeitschr. physik. Chemie*, 14, 155 (1894).

[4] *Zeitschr. physik. Chemie*, 11, 827 (1893).

[5] *Zeitschr. physik. Chemie*, 11, 492 (1893); compare also J. J. van Laar, *Ibid*, 13, 736 (1893).

[6] *Wied. Ann.*, 53, 209 (1894).

[7] *Zeitschr. physik. Chemie*, 20, 283 (1896).

[8] The greatest deviation from the mean was 3.1 millivolts.

[9] The greatest deviation from the mean was 3.8 millivolts.

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Sixth. More recently C. W. Kanolt[1] in examining the hydrolysis of the ammonium salt of diketotetrahydrothiazole, has found for the constant of dissociation of water at 25°, 0.82×10^{-14} and at 18°, 0.46×10^{-14}.

Seventh. H. Lunden,[2] in measuring the hydrolysis of the trimethylpyridine salt of *p*-nitrophenol has obtained at 15° C. the value 0.46×10^{-14}, and at 25° C., 1.05×10^{-14}. These correspond to about 0.61×10^{-14} at 18° C.

D. STANDARD SOLUTIONS AND THEIR MEASUREMENT BY THE ELECTROMETRIC METHOD; TABLE OF PRINCIPAL CURVES.

The standard solutions used in the colorimetric method and mentioned in the introduction are as follows:—

TABLE III.—GLYCOCOLL MIXTURES.

Composition of the mixture	Electromotive force π	Index of ions of hydrogen P_H^+
10.0 cc. glycocoll	about 0.6900	about 6.106
9.9 cc. glycocoll + 0.1 cc. HCl	0.5922	4.411
9.75 cc. glycocoll + 0.25 cc. HCl	0.5680	3.991
9.5 cc. glycocoll + 0.5 cc. HCl	0.5500	3.679
9.0 cc. glycocoll + 1.0 cc. HCl	0.5305	3.341
8.0 cc. glycocoll + 2.0 cc. HCl	0.5063	2.922
7.0 cc. glycocoll + 3.0 cc. HCl	0.4881	2.607
6.0 cc. glycocoll + 4.0 cc. HCl	0.4692	2.279
5.0 cc. glycocoll + 5.0 cc. HCl	0.4492	1.932
4.0 cc. glycocoll + 6.0 cc. HCl	0.4326	1.645
3.0 cc. glycocoll + 7.0 cc. HCl	0.4196	1.419
2.0 cc. glycocoll + 8.0 cc. HCl	0.4099	1.251
1.0 cc. glycocoll + 9.0 cc. HCl	0.4038	1.146
0.0 cc. glycocoll + 10.0 cc. HCl	0.3976	1.038
10.0 cc. glycocoll	about 0.6900	about 6.106
9.9 cc. glycocoll + 0.1 cc. NaOH	0.7883	7.809
9.75 cc. glycocoll + 0.25 cc. NaOH	0.8130	8.237
9.5 cc. glycocoll + 0.5 cc. NaOH	0.8325	8.575
9.0 cc. glycocoll + 1.0 cc. NaOH	0.8529	8.929
8.0 cc. glycocoll + 2.0 cc. NaOH	0.8780	9.364
7.0 cc. glycocoll + 3.0 cc. NaOH	0.8982	9.714
6.0 cc. glycocoll + 4.0 cc. NaOH	0.9228	10.140
5.5 cc. glycocoll + 4.5 cc. NaOH	0.9425	10.482
5.1 cc. glycocoll + 4.9 cc. NaOH	0.9763	11.067
5.0 cc. glycocoll + 5.0 cc. NaOH	0.9900	11.305
4.9 cc. glycocoll + 5.1 cc. NaOH	1.0050	11.565
4.5 cc. glycocoll + 5.5 cc. NaOH	1.0356	12.095
4.0 cc. glycocoll + 6.0 cc. NaOH	1.0531	12.399
3.0 cc. glycocoll + 7.0 cc. NaOH	1.0690	12.674
2.0 cc. glycocoll + 8.0 cc. NaOH	1.0795	12.856
1.0 cc. glycocoll + 9.0 cc. NaOH	1.0862	12.972
0.0 cc. glycocoll + 10.0 cc. NaOH	1.0916	13.066

[1] *Journ. Amer. Chem. Soc.* **29**, 1402 (1907).
[2] *Meddelanden fron Veteuskapsacademiens Nobelinstitut*, **1**, 8 (1907).

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1. N/10 hydrochloric acid (sometimes referred to simply as "HCl").

2. N/10 sodium hydroxide, (called "NaOH").

3. A N/10 solution of glycocoll to which NaCl has been added containing per liter 7.505 gr. glycocoll and 5.85 grams pure sodium chloride. (solution called "glycocoll").

4. A 1/15 molecular solution of primary potassium phosphate, 9.078 grams KH_2PO_4 per liter, (called "phosphate prim.").

Fifth. A 1/15 molecular solution of secondary sodium phosphate, 11.876 grams Na_2HPO_4 per liter, (called "phosphate sec.").

Sixth. A 1/10 molecular solution of secondary citrate of sodium, prepared by dissolving 21.008 grams of citric acid hydrate in 200 cc. of a normal solution of sodium hydroxide, and completing with water to 1 liter, (solution called "citrate").

TABLE IV.—MIXTURES OF PHOSPHATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. phos. sec.	0.8167	8.362
9.9 cc. phos sec. + 0.1 cc. phos. prim.	0.8092	8.171
9.75 cc. phos. sec. + 0.25 cc. phos. prim.	0.8015	8.038
9.5 cc. phos. sec. + 0.5 cc. phos. prim.	0.7914	7.863
9.0 cc. phos. sec. + 1.0 cc. phos. prim.	0.7790	7.648
8.0 cc. phos. sec. + 2.0 cc. phos. prim.	0.7616	7.347
7.0 cc. phos. sec. + 3.0 cc. phos. prim.	0.7500	7.146
6.0 cc. phos. sec. + 4.0 cc. phos. prim.	0.7402	6.976
5.0 cc. phos. sec. + 5.0 cc. phos. prim.	0.7308	6.813
4.0 cc. phos. sec. + 6.0 cc. phos. prim.	0.7210	6.643
3.0 cc. phos. sec. + 7.0 cc. phos. prim.	0.7109	6.468
2.0 cc. phos. sec. + 8.0 cc. phos. prim.	0.6977	6.239
0.1 cc. phos. sec. + 9.0 cc. phos. prim.	0.6787	5.910
0.5 cc. phos. sec. + 9.5 cc. phos. prim.	0.6608	5.600
0.25 cc. phos. sec. + 9.75 cc. phos. prim.	0.6438	5.305
0.1 cc. phos. sec. + 9.9 cc. phos. prim.	0.6248	4.976
0.0 cc. phos. sec. + 10.0 cc. phos. prim.	0.5990	4.529

Seventh. An alkaline solution of boric acid, prepared by dissolving 1/5 gram-molecule of boric acid (12.404 grams) in 100 cc. of N/1 sodium hydroxide and diluting to 1 liter, (solution called "borate").

These solutions were made with distilled water which had been boiled in timed copper vessels to free it from CO_2. The graduated flasks used, as well as the bottles in which the solutions were preserved were first of all filled with air free from CO_2.

(Here follow further precautions used in preparing the solutions and in testing the purity of the materials.)

In suitable mixtures of these standard solutions, the hydrion concentration was measured electrometrically as described above. Results are given in Tables 3 to 6. The first column gives the composition of 10

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cc. of the mixture. The second column gives the observed electromotive force, (π), of an element consisting of a calomel electrode immersed in N/10 KCl and a hydrogen electrode with the solution to be examined as the electrolytic liquid. The third column gives the value of the index of hydrogen ions (p_H^+) calculated from the electromotive force by equation, $p_H^+ = \frac{\pi - 0.3377}{0.0577}$.

The values given for π are the means of two or more frequently of a number of measurements made at different times, with different elec-

TABLE V.—MIXTURES OF CITRATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. of citrate	0.6238	4.958
9.5 cc. of citrate + 0.5 cc. HCl	0.6197	4.887
9.0 cc. of citrate + 1.0 cc. HCl	0.6164	4.830
8.0 cc. of citrate + 2.0 cc. HCl	0.6061	4.652
7.0 cc. of citrate + 3.0 cc. HCl	0.5943	4.447
6.0 cc. of citrate + 4.0 cc. HCl	0.5776	4.158
5.5 cc. of citrate + 4.5 cc. HCl	0.5655	3.948
5.0 cc. of citrate + 5.0 cc. HCl	0.5507	3.692
4.75 cc. of citrate + 5.25 cc. HCl	0.5413	3.529
4.5 cc. of citrate + 5.5 cc. HCl	0.5318	3.364
4.0 cc. of citrate + 6.0 cc. HCl	0.5092	2.972
3.33 cc. of citrate + 6.67 cc. HCl	0.4689	2.274
3.0 cc. of citrate + 7.0 cc. HCl	0.4488	1.925
2.0 cc. of citrate + 8.0 cc. HCl	0.4195	1.418
1.0 cc. of citrate + 9.0 cc. HCl	0.4054	1.173
0.0 cc. of citrate + 10.0 cc. HCl	0.3976	1.038
10.0 cc. of citrate	0.6238	4.958
9.5 cc. of citrate + 0.5 cc. NaOH	0.6275	5.023
9.0 cc. of citrate + 1.0 cc. NaOH	0.6325	5.109
8.0 cc. of citrate + 2.0 cc. NaOH	0.6443	5.314
7.0 cc. of citrate + 3.0 cc. NaOH	0.6590	5.568
6.0 cc. of citrate + 4.0 cc. NaOH	0.6821	5.969
5.5 cc. of citrate + 4.5 cc. NaOH	0.7030	6.331
5.25 cc. of citrate + 4.75 cc. NaOH	0.7230	6.678
5.0 cc. of citrate + 5.0 cc. NaOH	0.8600 0.9200	9.052 10.092
4.5 cc. of citrate + 5.5 cc. NaOH	1.0343	12.073
4.0 cc. of citrate + 6.0 cc. NaOH	1.0511	12.364

trodes and other solutions. The mixture eight parts glycocoll and two parts HCl was thus measured many times for the sake of testing the

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condition of the electrodes. As giving an idea of the agreement obtained, the set of 18 determinations is given:—

0.5064 0.5065 0.5049 0.5067 0.5063 0.5063 0.5064 0.5067 0.5057
0.5067 0.5070 0.5068 0.5064 0.5064 0.5065 0.5056 0.5052 0.5052

mean 0.5063.

The deviation from the mean is seldom greater than a millivolt, and generally much less. The author therefore believes that values of π given are within 0.001 volt of the true values.

TABLE VI.—MIXTURES OF BORATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. borate.	0.8709	9.241
9.5 cc. borate + 0.5 cc. HCl	0.8667	9.168
9.0 cc. borate + 1.0 cc. HCl	0.8620	9.087
8.5 cc. borate + 1.5 cc. HCl	0.8574	9.007
8.0 cc. borate + 2.0 cc. HCl	0.8517	8.908
7.5 cc. borate + 2.5 cc. HCl	0.8454	8.799
7.0 cc. borate + 3.0 cc. HCl	0.8384	8.678
6.5 cc. borate + 3.5 cc. HCl	0.8285	8.506
6.0 cc. borate + 4.0 cc. HCl	0.8160	8.289
5.75 cc. borate + 4.25 cc. HCl	0.8072	8.137
5.5 cc. borate + 4.5 cc. HCl	0.7958	7.939
5.25 cc. borate + 4.75 cc. HCl	0.7774	7.621
5.0 cc. borate + 5.0 cc. HCl	0.7155	6.548
4.75 cc. borate + 5.25 cc. HCl	0.4745	2.371
10.0 cc. borate	0.8709	9.241
9.0 cc. borate + 1.0 cc. NaOH	0.8778	9.360
8.0 cc. borate + 2.0 cc. NaOH	0.8860	9.503
7.0 cc. borate + 3.0 cc. NaOH	0.8960	9.676
6.0 cc. borate + 4.0 cc. NaOH	0.9132	9.974
5.0 cc. borate + 5.0 cc. NaOH	0.9768	11.076
4.0 cc. borate + 6.0 cc. NaOH	1.0518	12.376

It will be noted that in measuring the more acid and more alkaline of the solutions it has been necessary to make corrections, whose magnitude and algebraic sign agrees perfectly with what has been said before on the subject (pages 145 and 149). In these cases it is the corrected values of π which are found in the tables.

Chart of Principal Curves.—The curves called on the chart "glycocoll + hydrochloric acid," etc., have for abscissas the values of the exponent of the hydrogen ions p_H^+, shown in the last column of Tables III-VI, and for ordinates the content of the mixture in glycocoll, citrate, borate and secondary phosphate respectively.

Further, the chart contains the line of the exponents of hydrogen ions which, as has been said, permits one to determine graphically the value of p_H^+ corresponding to a π measure, and inversely.

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By the aid of the curves the values of π and p_H^+ may be found for all mixtures of the standard solutions, in question, even those not given in the tables. Suppose, for example, we wish to find these values for the mixture 8.6 cc. of glycocoll + 1.4 cc. HCl. Find the ordinate 8.6 and follow the horizontal line 8.6 to its point of intersection with the curve glycocoll and hydrochloric acid. The abscissa of this point is 3.15, a number which therefore represents p_H^+ of the mixture.

Values of π for intermediate proportions of mixtures were taken from the chart, and afterward π was measured electrometrically for these same mixtures, the values thus found differing by less than 1 millivolt.

The close agreement between values of p_H^+ deduced from the curves and those for the same mixtures electrometrically determined supports the belief of the author that the values of π given in the tables are not subject to an error of more than 1 millivolt. The dotted parts of the curves are those which are not available for determining values of π or p_H^+. Since a change in the ordinate of a curve corresponds to a change in the composition of a mixture, and a change in the abscissa denotes a change in the hydrion concentration, it is evident that where the curve is nearly or quite parallel to the axis of abscissas, it could not be used, because a very minute change in the composition of the mixture corresponds to a great or even very great change in the ionic concentration.

Solutions of glycocoll which had been kept for some months did not show constant values for π. This fact the author attributes to minute impurities in the solution. The same behavior was observed on the part of those solutions containing small proportions of NaOH and HCl mixed with glycocoll. For this reason the curve of glycocoll and HCl is dotted from 10 cc. glycocoll to 9.5 cc. glycocoll and 0.5 cc. HCl, and that for glycocoll and NaOH from 10 cc. glycocoll to 9.75 cc. glycocoll and 25 cc. NaOH. For similar reasons parts of the other curves are dotted. The primary phosphate for instance gave the same value of π after nine months, while in the case of the secondary phosphate the value of π had decreased in the same time 8 millivolts.

(To be continued.)

Chrome Tannage. E. GIUSIANA. *Collegium*, No. 444, p. 33, 1911.—The author prefers in general the one-bath method on account of its greater economy and the greater certainty of results. For leathers where a soft texture and finish are desired, the two-bath process has decided advantages, however, because the sulphur deposited in the leather by the decomposition of the hyposulphite of soda of the reducing bath tends to make the finished leather smooth and supple. The maximum quantity of sulphur found was 0.7 per cent.

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The author thinks that there is no essential difference in the result in the one-bath and two-bath processes, from a chemical point of view. The essential feature, he says, is the fixation of oxide of chrome on the hide-fiber by the dissociation of easily broken up basic salts of chrome by catalytic action on the part of the hide in contact with the chrome salt. He remarks that this dissociation may be seen in the case of very basic salts simply by diluting the chrome solution with water. The maximum quantity of Cr_2O_3 fixed by the hide is 6 per cent.

The author states that the chrome salt employed to the best advantage in one-bath tannage is chrome alum, rendered basic with solvay soda. In order to prepare a bibasic chrome salt, equimolecular quantities of alum and soda are taken:—

$$K_2Cr_2(SO_4)^4 + Na_2CO_3 + H_2O = K_2SO_4 + Na_2SO_4 + Cr_2(SO_4)^2(OH)^2 + CO_2.$$

If two molecules of soda are used for each molecule of alum, a tetrabasic salt is produced.—

$$K_2Cr_2(SO_4)^4 + 2Na_2CO_3 + 2H_2O = K_2SO_4 + 2Na_2SO_4 + Cr_2(SO_4)(OH)^4 + 2CO_2.$$

The latter solution tans better, but the author prefers to start the tannage with a less basic salt and add more soda a little at a time as the process goes on, stating that this method gives a finer, firmer grain.

The bichromate of sodium and sodium chrome alum possess an advantage because it is easier to wash the sodium salts out of the leather. The author prefers in making chrome liquors from sodium bichromate to make a stock liquor of 28 to 30° Bé. He does not employ sulphurous acid, but an organic reducing agent, preferring glycerine to sugar. The action of the glycerine is very violent, and the chemical reaction very complex, glyceric and tartronic acids and formaldehyde being among the products.

The analysis of a basic liquor thus prepared, at 30.6° Bé, was, water 71.1 per cent., $Na_2Cr_2O_7$ 12.16, H_2SO_4 14.69, NaCl 0.13, organic matter 1.91.

The basicity of the liquor varies according to the quantity of sulphuric acid used in the reaction.

A table is given showing quantities of soda required to convert various quantities of chrome alum into basic liquors of varying degrees of basicity. One lime of the table gives the proportions for all, 1 kg. of crystallized chrome alum corresponding to 294.5 grams of potassium bichromate or to 152.5 grams of Cr_2O_3, requires 50 grams of dry Na_2CO_3 to convert it into the monobasic salt, 100 for the dibasic, 150 for the tribasic and 200 for the tetrabasic. A second table shows the quantities of pure sulphuric acid and glycerine required to convert various quantities of potassium bichromate into basic salts. Here again one line gives proportions for all. 1 kg. of crystallized chrome alum containing 393 grams H_2SO_4 corresponds to 294.3 grams of $K_2Cr_2O_7$. To reduce this to the tetrabasic salt requires 207 grams of

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sulphuric acid; to the tribasic, 254 grams to the dibasic, 299.5 grams and to the monobasic 347.5 grams, the quantity of glycerine at 28° Bé in each case being 98 grams.

Chrome Tanning. From *Le Marché des Cuirs*, 1911, (33), No. 1, pp. 1-2.—The following experiments have been made on the drums for the first and second baths, with sheepskins passed through a bran bate. There are several modifications in the process of chrome tanning in two baths. In the first place, the first bath may be made of bichromate, of salt and hydrochloric or some other acid, or alum may even be added. The second bath may be made of hyposulphite of soda, of salt and hydrochloric acid, or some other acid. Sulphites may also be used for the second bath. To simplify matters but two cases will here be considered. First case:—A bichromate bath without alum and a reduction bath of hyposulphite of soda. Second case:—A bichromate bath containing alum and the same reduction bath as above. The acid used is hydrochloric at 21° Baumé. *First Case.* The bichromate bath was made with bichromate of potassium, salt and hydrochloric acid. This liquid was kept as fresh as possible in order not to shrivel the skins. The skins were turned three hours in this first bath and were taken out over night. The second bath was used twice, first very dilute and of short duration, and then normal, the acid being diluted to five or six times its volume with water and added at the axis of the drum during the process. In this last bath the skins were examined at very short intervals after the addition of the acid to keep track of the process of the change in color.

After the first hyposulphite bath, the skins were of an old gold color and dripped strangely; that is the least pressure made the yellow solution due to the bichromate, run out, since only the surface of the skin had undergone a slight change. The second hyposulphite bath was first set up with the whole quantity of hyposulphite and salt, and one-sixth of the acid. The remainder of the acid was added one-sixth at a time every five minutes.

Five minutes after the addition of the third sixth of the acid (½ of the whole amount) the skins were of a greenish color, still verging on yellow.

Five minutes after the addition of the fourth sixth (*i.e.* 2/3 of the acid and 20 minutes of drumming) the skins had become putty color with still a faint trace of yellow.

Five minutes after the addition of all the acid the skins were green, that is completely changed, and the liquid obtained by pressure contained no trace of yellow. When a skin was cut, the inside, naturally was yellow. After 2½ hours of drumming (three hours in all) the hides were taken out on a rack. At this time a cut in the thick neck pieces still showed a tiny yellow gray line. This trace had disappeared after 24 hours on the rack. The tanning was finished.

Second Case. The bichromate bath was made up with bichromate

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of potassium, salt, alum and hydrochloric acid. The skins were turned in this bath three hours and taken out over night.

For the second bath two hyposulphite baths with the same proportions of acid added in the same way were used. In this case the color change is much more rapid than in the first case, which is due no doubt to the sulphuric acid contained in the alum settled on the skins. After the first hyposulphite bath, the skins were already of a greenish yellow color. In the second hyposulphite bath the change of the surface of the skin was complete when the bath contained half the whole quantity of acid. This indicates that by this process the loss of chrome is less to be feared. As in the preceding process the tanning is completed on a rack.

Extraction of Tanning Materials. J. R. BLOCKLEY. LEATHER, II, 21, Jan. 12, 1911.—The object in leaching is to get the tannin from the material with the use of as little water as possible. In order to get all the tannin, much water must be used and the solution obtained would be too weak for use. The tannin is extracted by diffusion from the cells of the bark or wood through the cell wall into the surrounding liquor, and it is only when the liquor is weaker than the solution in the cells that tannin passes into the liquor from the cells. The same principle holds in the relations between the liquor and the hide, so that a hide will only tan in a liquor stronger than the infusion of tannin already in the hide. The writer summarizes his conclusions thus:—

1. It is impossible to extract materials well in one extraction.
2. It is unwise to bring strong liquor in contact with nearly spent material.
3. Water must be used only on nearly spent material.
4. Hides should not be kept long in a liquor of the same strength and should not be put from a stronger liquor into a weaker one.

Substitute for Platinum Triangles. R. C. BENNER. *Jour. Amer. Chem. Soc.*, 33, 189, Feb., 1911.—The writer has tested an alloy of chromium and nickel called nichrome for making wire triangles to support crucibles. He finds the nichrome triangles very resistant to heat and corrosion. The cost is about the same as that of pipe-stem triangles. They may be obtained from H. C. Stoelting & Co., Chicago.

Mangrove Bark Industry for Australia. From Vice-Consul H. D. Baker, Sydney, through *Shoe and Leather Reporter*.—It is said that the supply of black mangrove trees in Northern Australia is practically unlimited. A company has been organized to market the tanning materials in the form of solid extract. Some of the trees furnish logs 50 feet long and more than a ton of bark has been taken from a single tree The bark yields from 45 to 54 per cent. of its weight in solid extract An analysis of the bark made in Sydney gave tannin 38.2 per cent., non-tan 8.1 per cent., water 9.8 per cent.

Mangrove furnishes a tanning material easily soluble, cheap, and

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satisfactory in every respect except that it gives a red color to the leather. This difficulty can be overcome as has been shown by experiments at the Sydney Technical College.

Method of Estimating the Acidity of One Bath Chrome Liquors. MORRIS BATESON, in LEATHER, 2, 263, Dec., 1910.—The addition of ammonia to a one-bath chrome liquor precipitates the chromium as hydroxide, the acid combining with the ammonia. The addition of formaldehyde forms hexamethylene tetramine and liberates the acid, which may then be titrated with N/2 caustic soda, using phenolphthalein as indicator.

The following procedure has been found convenient: to 50 cc. of the liquor (containing from 0.5 to 1.0 per cent. Cr_2O_3) ammonia is added until phenolphthalein is reddened. The sample is then made up to 100 cc., shaken and filtered. The filtrate should be pink from the phenolphthalein. To 50 cc. of the filtrate 10 cc. of 40 per cent. neutral formaldehyde is added, and titrated with N/2 caustic soda. Each cc. of soda = 0.024 gram SO_4 or 0.01775 gram Cl.

A table of results is given in which new chrome liquors show results almost the same as those obtained by titrating the boiling chrome liquor direct with N/2 NaOH. The method does not work well on old liquors, as the formaldehyde acts on dissolved hide substance to form acids.

The Dyeing of Chrome Leather. HUGO KUHL. *Ledertech. Rundschau,* 1910, pp. 394-5.—The practical problem for solution was to make a hard, parchment like split leather soft and elastic and to dye it. A successful method was worked out as follows: The excess of chromium salt was leached out with water at ordinary temperature and the leather was then soaked 2 hours in dilute HCl (1 liter 42 per cent HCl in 100 liters water) and afterward treated 3-4 hours in a concentrated soap dyeing bath, which may be used continuously on renewal each time with a little soap. The ordinary soaps used in the tannery were employed and it was found that castor oil and whale oil soaps containing excess of fat could be used. The dyed leather was fixed in 5 per cent. solution of sodium thiosulphate which is re-strengthened from time to time. With acid violet and fast blue (Badische Fabrik) a soft strong leather in bright colors was obtained, fast to soap and washing.

In another process the chrome leather first treated as above was further treated in a conc. soap bath 3-4 hours at 65° best in washing or dyeing drum. The leather then went direct into the dye-bath which contained 5 per cent. sodium thiosulphate; the dyeing was complete in 24 hours at ordinary temperatures. This gave a handsome bright leather, but not so soft as by the first process.

This process according to the author, is founded on the fact that oxidation plays an important part in tanning. Modern investigations

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justify to some extent the theory of Knapp that tanning is a form of dyeing. Here the tanning agents are the soap (chamoisage) and the dyestuff. On the basis of these researches, the affinity of coal-tar dyes for leather would seem not to be so slight as stated by Lamb.

W. J. K.

Colloids; Studies on Organic——. S. LEVITES. *Z. Chem. Ind. Kolloide,* through J. S. C. J., 1910, **8**, 4-8.—Glutin is insoluble in cold water but dissolves tolerably easily in solutions of iodides and thiocyanates. Casein, which is insoluble in warm water, yields a stable opalescent solution. which can be readily filtered, when it is triturated with saline solutions (potassium iodide, sodium thiocyanate, sodium phosphate, potassium nitrate) and the mixture warmed. The casein is precipitated from the solution on addition of acid. Gliadin does not behave in an analogous manner. Glutin and casein are both insoluble in pyridine, but in aqueous pyridine the solubility increases with the pyridine content up to a maximum for the mixture, $C_5H_5N + 2H_2O$. The casein solutions are precipitated by addition of more pyridine or by strongly diluting with water, but the glutin solutions are unaffected by such treatment. The solutions in aqueous pyridine are very viscous. Glutin and Witte peptone are readily soluble in formamide, giving transparent, very viscous solutions, which are unaffected by dilution with water; the glutin shows no tendency to gelatinize even in concentrated solutions. Casein dissolves only in traces, and gliadin is quite insoluble in formamide. The precipitation of proteins by tannin is a more sensitive reaction than the biuret reaction, glutin can be detected at a dilution of 1 : 15,000, egg albumin at 1 : 800, and Witte peptone at 1 : 5000. In a series of tests in which pieces of gelatine were swollen in water then placed in contact with tannic acid solution, it was found that more tannic acid was adsorbed the longer the gelatine was previously soaked in water. Gelatine which had not been soaked adsorbed very little tannic acid. Considerably more tannic acid was adsorbed in presence of an electrolyte. By using a sufficient excess of tannic acid, gelatine can be quantitatively precipitated; the precipitation is favored by hydrogen ions, but hydroxyl ions act injuriously. The tripeptide, leucyl-glycyl-glycine, in 3 per cent. aqueous solution, is not precipitated even by a considerable excess of alcohol, but is precipitated immediately on addition of 1/40 vol. of ether.

Leather Rendement and Examination. W. APPELIUS AND L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, pp. 385-6, 393-4, 401-3.—In this work are reported the conclusions from many analyses of vegetable tanned leather.

In leather analysis, the nitrogen content is of especial value: from this the degree of tannage may be computed. Dry hide substance of the hide of cattle or horse contains 17.84 per cent. N, or 1 part N = 5.62 hide substance. The addition of the N-free tannin to the hide therefore lowers the ratio of N and the lower the percentage of N, the

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better the tannage. The following analysis of a North German sole leather is a type:

	Per cent.		
Water	18.0	Leather substance:	
Minerals	0.6	Fixed tannin	32.4
Fat	0.4	Hide subst	39.7
Solub. organ. matter	9.3		
Leather subst	71.7		71.7
		Per cent. N in leather	7.0
	100.0	Rendement number	254.4
		Tannage number	82.4

In this, according to von Schroeder's methods, the rendement and tannyl numbers represent the amounts of air dried leather and tannin respectively to 100 parts of hide substance. Von Schroeder also reckoned the approximate rendement based upon green or white weight, assuming that 125 parts green hide or 100 parts white hide = 28 to 31 parts dry hide substance. The authors, however, maintain that reliable valuation of the yield cannot be derived from the rendement and tannage numbers alone since the yield does not wholly depend upon the tannage. The principal additional elements which affect the rendement are: (1) Correctly stated green weight; (2) Location of the hide sample; the greater the surface of the hide in proportion to the weight, the greater the proportional loss in offal and hair as shown by the following yields out of the same lot of leathers of uniform tannage:

Thickness below 3.5 mm.		Thickness, 3.5-4.5 mm.	
Lbs. crude wt.	Per cent. yield	Lbs. crude wt.	Per cent. yield
50-59	56.9	60-69	54.1
60-69	52.0	70-79	53.2
70-79	50.7	80-89	51.9
		90-99	48.9

(3) The preliminary treatment of the hide, especially in fixing the white weight, of which the rendement may be 72-75 per cent. with the more shrunken sulphided hides, 82-85 per cent. with the more swollen limed hides. (4) Variations in the sticking.

None of these are taken account of in the analysis, hence it is not correct to refer it to the green or white weight. Von Schroeder's ratios were derived by investigation of the same hide from the green state to finished leather but in the tannery or laboratory this in general cannot be done and the computation of even the approximate rendement according to von Schroeder's rules is irrational. This is demonstrated by the following table giving the results obtained by the author with 6 pit tanned vache leathers of uniform tannage:

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	(1)	(2)	(3)	(4)	(5)	(6)
Green weight, lbs.	70	70	76	72	64	72
Soft weight, lbs.	76	72	77	78	64	72
White weight, lbs.	59	63	64	63	53	60
Leather weight, lbs.	34	35.5	36	37	30	32
Leather rendm., %, factory	48.6	50.7	47.4	51.4	45.6	44.4
Leather rendm., %, analysis	61.1	64.2	63.2	63.7	64.4	65.5
Leather rendm., %, difference	12.5	13.5	15.8	12.3	18.8	21.1
Thickness leather, mm.	3.5	4.5	4	4	3.5	3.5

Further, in the practice of the Freiberg Tanning School, 50 different lots of hides were compared; the rendement limits were 45.7 and 59.3 per cent. of green weight according to the quality, all the same tannage, averaging each lot; individual hides showed differences of 23 per cent. By analysis the limits in rendement were 61.1 and 65.6 per cent. showing practically uniform tannage considering the approximate character of the analysis and the uncertainty of sampling. The analysis therefore does not distinguish these leathers or properly return the factory rendement.

It is extraordinarily difficult to sample fairly for analysis The various parts of the hide give different rendement figures, the butts the lower and the sides the highest; the looser hide taking up the most tannin, gives highest rendement and the hide of finer texture, the lowest. In actual manufacture, the reverse is the case; the loose hide gives the lowest rendement because as wet hide it holds much more water and contains less hide proportionately; this counts in the determination of the green weight and still more with the white weight. The relations existing in actual practice were illustrated by the following experiments. Various hides after liming were cropped and the relative weights of butts and offal determined. After tannage in pits the ratio of the leathers was likewise determined.

	Per cent. pelt of green wt.	Pelt		Leather	
		Butts	Offal	Butts	Offal
Cow 2	84.5	41.1	58.9	45.1	54.9
Ox 4	84.4	40.0	60.0	49.1	50.9
Bull 6	83.5	36.5	63.5	45.2	54.8

The table shows decidedly that more leather is obtained from the pelt of the butts than the waste whereas by the analyses less leather was always obtained.

It is almost impossible to secure an average sample. In the tannery, one is limited to a single hide which may accidentally greatly vary as shown in the following table of yields from large lots of dealer's hides published in the Freiberg Tanning School Report for 1905-6.

	Crude weight Lbs.	Soft weight		White weight	
		Lbs.	Per. ct.	Lbs.	Per ct.
Best lot (15 hides)	1,092	1,047	95.9	875	80.1
Poorest lot (15 hides)	978	882	90.2	741	75.8

The analyses reported in the tables A, B, C below show the great

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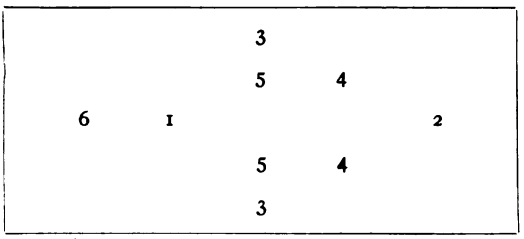
variations in yield according to the parts of hide taken. These were



located as follows: (1) back (near rump), (2) neck, (3) belly, (4) neck-base, (5) mid-bend, (6) root of tail. Table A shows that

TABLE A.—PIT TANNED LEATHER.

	1 Back	2 Neck	3 Belly	4 Neck-base	5 Mid-bend	6 Tail
First Layaway:						
Cow						
Rendement number	253.5	260.4	278.2	252.6	262.1	259.8
Tannage number	83.5	87.5	92.3	83.7	85.7	87.1
Organic solubles	8.3	8.7	11.4	8.0	10.2	8.5
Fixed tannin	33.0	33.6	36.0	33.2	32.4	32.8
Ox						
Rendement number	269.2	273.2	292.4	268.1	274.5	264.5
Tannage number	95.0	95.2	103.4	90.7	95.1	89.3
Organic solubles	8.2	8.9	10.8	9.4	9.0	8.8
Fixed tannin	35.3	34.8	35.4	33.9	34.6	36.2
Bull						
Rendement number	250.0	260.8	289.2	267.4	269.2	262.1
Tannage number	78.2	85.0	101.6	91.4	89.0	86.4
Organic solubles	9.2	9.6	10.6	8.9	10.3	9.5
Fixed tannin	31.3	32.6	35.2	34.2	33.1	35.0
Second Layaway:						
Cow						
Rendement number	261.8	283.0	292.5	279.6	281.3	279.8
Tannage number	85.6	93.3	97.7	94.0	96.1	101.1
Organic solubles	9.7	12.2	13.2	11.2	10.8	9.0
Fixed tannin	32.7	32.8	34.0	33.4	34.2	33.8
Ox						
Rendement number	277.8	278.2	283.4	274.3	271.4	262.1
Tannage number	96.9	99.3	92.3	91.7	87.9	87.1
Organic solubles	9.6	8.9	12.6	10.7	11.3	9.3
Fixed tannin	34.1	35.7	32.6	33.4	32.4	33.2
Bull						
Rendement number	258.7	279.8	283.4	274.3	271.4	262.1
Tannage number	88.0	90.9	92.3	91.7	87.9	87.1
Organic solubles	8.0	12.0	12.6	10.7	11.3	9.3
Fixed tannin	34.0	32.5	32.6	33.4	32.4	33.2

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the rendement and tannage numbers are least in the back and confirm Paessler's prescript for taking the neck as best average. The middle piece (5) between the belly and the back is also seen to give average values. These are recommended, however, only in case but *one* sample may be taken.

TABLE B.

	Pit tannage					Drum tannage		
	Cow 1	Cow 2	She-calf	Ox	Bull	Cow	Ox	Bull
Rendement number	277.5	270.9	264.4	269.4	273.0	261.3	256.9	256.6
Tannage number	99.2	96.2	94.4	92.2	96.6	97.8	96.2	95.4
Organic solubles	8.8	8.2	7.0	9.4	8.8	5.0	4.1	4.3
Fixed tannin	35.7	35.5	35.7	33.9	35.0	37.3	37.9	37.3

In Table B (here condensed to averages from head, neck and belly) are compared pit tanned and drum tanned leather. The solubles in the last (which was to be sure very thoroughly washed) are the lowest throughout, but the fixed tannin highest which is probably due to the leather coming quicker into concentrated liquors in the drum

TABLE C.—PIT TANNED VACHE LEATHER.

Handlers	1	2	3	4	5	6	7
Rendement number	256.0	251.7	356.8	258.9	256.0	256.8	244.5
Tannage number	85.3	85.1	85.5	86.5	86.4	83.5	82.0
Organic solubles	7.9	7.1	8.3	8.5	7.7	8.9	5.9
Fixed tannin	33.4	33.7	33.3	33.5	33.7	32.5	33.9
"Versenk"							
Rendement number	256.9	258.3	259.9	256.7	257.5	263.5	254.5
Tannage number	82.0	81.6	84.2	82.8	83.1	90.7	80.9
Organic solubles	9.7	10.1	9.6	9.3	9.2	8.2	9.1
Fixed tannin	31.9	31.6	32.4	32.3	32.4	34.4	31.8
Layaway							
Rendement number	259.1	272.0	267.8	269.8	273.0	277.8	264.0
Tannage number	80.6	88.2	85.1	85.8	87.6	90.3	81.8
Organic solubles	10.7	11.1	11.2	11.4	11.6	11.7	11.6
Fixed tannin	31.1	32.3	31.8	31.7	32.1	32.5	31.0

Table C (condensed) gives the analysis averages of 7 vache leathers each time out of the handlers, "versenk" and layaway. In the Tanning School the leather remains a long time in the handlers and is then already well tanned as the analyses show. After this the increase in weight is largely due to extractable substance, but the leather becomes more solid in the "versenk" and layaway.

The authors promise further studies in this direction, one being a member of the commission on leather analysis chosen at the International Congress held at Paris in September.

The Measurement of the Color of Tanning Extracts. W. EITNER. *Der Gerber.* 1910, (36), 321-3.—In recent times since the introduction of

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clarifying processes in extract manufacture, account has been taken of the color in the valuation of extract. Experience has shown that a light colored extract not only gives light colored leather but tans better and quicker and is better utilized. The principle of the colorimetric method by the Lovibond tintometer mostly employed in England consists in matching the color of the extract by a sufficient number of super imposed standard glasses of the ground colors, yellow, red and blue. Professor Procter has improved the method by employment of spectral absorption. In Europe these optical methods are not employed in commercial analysis, but empirical methods by comparison. Dr. A. Gansser in Garessio has devised such a method whereby the coloring effect of the extract may be observed upon animal fiber. An artificial hide "animalized cotton," is prepared from the so-called bachet which is felted on one side and fine wove on the other. This material, 1 mm. thick, is cut in strips 11 cm. wide, 20 m. long and rolled on spools. In a suitable apparatus the material is reeled through boiling water, then pressed by a roll and run through ¼ per cent. formaldehyde solution and from this through a 6 per cent. solution of pure gelatin at 60-65° C.; an attachment scrapes off the excess of gelatin. The dried material is quite stiff, pure white and can be preserved indefinitely in rolls. For tanning experiments, 2 pieces are cut of 2½ grams weight each and softened in water. In testing extracts, 10 cc. of 25° B. with 30 cc. water yielding a liquor of 6° B. are used; for difficult soluble quebracho extracts, 3° B. liquor is taken. The softened strips are placed in the liquor in glass cylinders and shaken for 12 hours at 25 revolutions per minute when the tannage should be complete. The tests are then rinsed 10 min. in running water, pressed and dried like leather, first at room temperature, then at 30°. They may be made smooth by pressing, but ironing, even at moderate warmth, affects the color to some extent.

The author has tested some of Dr. Gansser's original material with very satisfactory results; the shade and depth of color corresponded well with parallel results on hide. As to the reputed uncertainty of tests with hide skivers, etc., the author has found that sufficient regularity in grain coloring may be secured with care. The pelt should be thoroughly cleansed, accurately delimed to neutrality and well dickered, it is then pickled and preserved for use and will keep for months. Before use it is neutralized and well washed to free from salt. The chief advantage of the cotton test is in its rapidity since a hide test requires several days. The author is not of the opinion that this method will enable one to judge the effect of the extract upon rendement and solidity of the leather as Dr. Gansser suggests, but the light proof character of the colors may be determined much more rapidly than with leather. In this way the rapid darkening of colors from sulphited extracts as compared with those from genuine decolorized extracts was observed after exposing a few days to the light.

The optical method, especially with Procter's improvement, seems best suited for control in extract manufacture. It would be well to set the

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standards by extracts which had been controlled by tests upon animalized cotton. For the consumers, the dyeing test direct would be preferable.

Chrome-Chamois Glove Leather. B. KOHNSTEIN. *Gerber-Courier. Jubiläums-Ausgabe,* 1910, pp. 36-7.—While the chamois leather manufacture is confined to a few manufactories which produce a high grade product, in America this industry is increasing and with considerable export. The American glove leather is not, however, a genuine chamois but an imitation, the so-called chrome-chamois leather. The native inventiveness of the Americans and their striving toward home production of all necessities, have perfected this manufacture. Live stock in America is exposed to barb wire fencing and the resulting scars on the skins as well as other blemishes are easiest disguised in this form of leather. In the manufacture the hides must be well softened and cleaned. Stale soaks are shunned for it is necessary in chrome tannage to preserve hide substance in all stages of the beam house work; with dry hides, 1½ per cent. salt is added to the soaks of the second day followed by fresh water the third day. The hides are milled in fresh water before liming. Cattle and horse hides are limed 2 days with addition of arsenic, then 6 days in pure lime. Dog and sheepskins need longer liming to avoid natural fat spots which are troublesome with the light shade dyes. After unhairing, fleshing and scudding, a bran drench with addition of a little pigeon dung is of advantage. The pickle for 100 kg. white pelt consists of 40 liters water, 36 kg. salt, 4.5 kg. sulphuric acid. For a second lot of hides, it is strengthened with half the amounts of chemicals. The acid strength must be regularly controlled by the chemist. After pickling, the moisture is pressed out by rollers and the hides are split, then drummed with 3 per cent. salt solution and are then ready for the double chrome bath. For the reducing bath, to 1 kg. pelt, 0.16 kg. sod. thiosulphate, 0.08 kg. HCl and 2 liters water are used. The leather is milled with this 3½-4 hours, let stand over night and milled again 1 hour. It is then treated ½ hour with 2 per cent. borax solution at 40° C. and rinsed in warm water, then pressed, shaved and leveled.

The fat liquor, containing 1.33 water, 2.5 neutral oleate, 4.0 sod. oil chrome-moellon, and 1.2 per cent. borax (sic) is milled with the leather for 30 minutes at 45° C. After drying, the leather is layered grain to grain in sawdust containing 35-40 per cent. water and left under weights for 12 hours. Various machine work follows including a buffing with carborundum. Dyeing is applied by dusting on the table; fine pipe clay is mixed with water, toned for gray with logwood and acetate of iron, or colored to pale yellow with willow and fustic. In order to give the chrome chamois the natural looseness of genuine chamois, the chrome bath is made strong; for 1 kg. pelt, 0.8 kg. bichromate, 0.4 kg. HCl of 22° B., and 1.27 liter water used, milling 3-4 hours. Heating is avoided, else a brittle chrome glue results. The hides are spread smooth over

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horses avoiding creases which are sure to show later. Exposure to sunlight is avoided which may cause local reduction.

Glove Leather Manufacture. *Ledertechn. Rundschau,* 1910, pp. 395-7, 404-5, 400-11.—The crude material for glacé leather must be tender, clean grained kid and lambskins from animals still fed by the mother or at least only partially on solid food. Together with the lambskins yearling and sheepskins of the better sorts are used also.

(A) *Lamb Leather.*—The crude skins are carefully sorted by special workmen trained by long experience. After rejecting all skins with dull, dirty or thick flesh or other defects, the sorting is made into primes, seconds and thirds which are minutely described; these are further graded by age. Equivalent lots for working are:

	Sucklings	Lambs	Yearlings
Small	1,400	1,000	650
Medium	1,250	900	600
Large	1,100	800	550

All the skins in each lot must be from the same source which is the care of the sorter.

In the management of the soaks regard is paid to the origin of the skins, whether they be freshly dried or long stored, the season of the year, etc. The softening is complete when all parts of the skin may be equally stretched in both directions. Too long soaking, however, extracts hide substance and gives a flabby leather without strength or gloss and in extreme cases, decay begins and the final leather is brittle and inelastic. With too short a soaking, only the softened parts are loosened and plumped in the limes and the leather lacks in elasticity. If the water is not changed often enough, the blood is not extracted and instead of white, the leather is gray and without gloss. The use of soaks a second time is to be condemned. The normal time is 2, at the most 4 days, with change of water every 12 hours.

The liming likewise should be neither too long nor too short. Old, stale limes are strictly excluded; they produce spongy leather with wrinkled grain. If the swelling in the lime be too lengthy, the fiber does not go back again; the leather is spongy and when pulled, the grain draws up in folds. Too short of too weak liming results in completely inelastic leather. For preparing and bettering the limes, lime that has been stored not less than 2 months after slaking should be used, its action being much milder. In slaking, water is added until there is a permanent layer over the lime. The addition of arsenic to the lime hastens the loosening action and gives gloss to the grain; it also hems the swelling action. An excess injures the wool and still more the tender hide fiber. A lime liquor should not be used over 2-2½ months according to season. The duration of liming for mild natured ware is 8 days at the least, 12 for hard ware and 18 for very hard imported stock. Heed must be given that the temperature be uniform as possible. The apparatus should therefore be under cover in rooms with cool ventilation

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in summer and heat in winter. The proper temperatures are 16-19° C. for the liquor and 20-22° for the room. Warming of the liquor does not accomplish the same result as a room of uniform temperature and there is too much variation. The lime vats should be capacious, 50 hectoliters to 900 lambskins with 36 hl. liquor so that the skins swim and are not jammed. The quantities for bettering are computed not from the volume of the liquor but from that of the skins; this is measured by observing the increase in depth of the liquor on immersing the hides and this multiplied by the cross section of the vat gives the volume or cubic contents of the hides. For each hectoliter, 4½-5½ liters thick slaked lime are reckoned and to 100 liters of slaked lime, 2½-3 kg. red arsenic. This is for wool skins; shorn skins take a third more in lime and arsenic. The specified quantities include the total additions (made every other day) for the entire period of liming. For soft hides, the minimum of lime and maximum of arsenic are used, for hard hides, the reverse. For freshly preparing a lime in a vat of 2 × 1.7 × 1.5 m. (liquor 1.3 m. deep) 50 liters thick slaked lime are used. The skins are well drained from the soaks and put in the limes. The next day they receive the first bettering, are turned daily and bettered every other day. When handling, the skins must be thoroughly agitated in the liquor to loosen any deposits of lime.

The subsequent cleansing work must proceed gradually nor should the skins ever go into cold water which shrinks them and makes the removal of lime and dirt difficult or even impossible. On the other hand there should be no delay: 3-4 days from the lime to the bran drench are enough at the most; else putrefaction may begin. The skins are taken in the morning from the lime, drained till afternoon, then thoroughly washed in tempered water (lime temperature) to which a few pailfuls of clean lime liquor have been added. The washing vat is drained, refilled and the above operation repeated. The skins are finally left in a third water over night. The wool is removed the next day, round, polished irons being used; great care is given to this work. The skins then go direct from the beam into tempered water clouded with lime liquor and are well rinsed. Trimming follows and only the coarsest flesh is removed, the real flesh being left for protection during bating. After standing in water over night with renewed agitation the next morning the water is mostly drawn off and the fells are worked or lathered ("gegascht") for 15-20 minutes, then rinsed and piled for bating.

The object of the puer is to remove the remaining lime scum and other dirt. For 100 medium lamb fells, 7-8 liters of dog dung paste which has fermented 2 weeks is used. This is diluted with sufficient hot water that it may run through a fine sieve, the residue being washed again. The whole is further diluted with warm water so it may be filtered through coarse lime. The filtrate is diluted then in the puering vat and regulated to 22½° C. The fells are driven ½-¾ hour, let rest one hour and driven 10 minutes and so on 3½ hours for light fells.

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heavier 10 hours. The desired effect is reached when the flesh is easily stripped off by the finger nail. The flesh is then removed on the beam, and the fells placed in a little water and lathered for 15-20 minutes. This is repeated with fresh water, the fells then rinsed, stacked, drained and laid in tempered water. Without delay they are worked on the grain with polished irons, lengthwise of the back and across the sides. Washing, lathering and rinsing follow, then a second scudding of the grain and the fells go directly to the drench.

For 100 medium lamb fells, 1 kg. wheat bran is reckoned; this is softened 2-3 hours in cold water, then washed twice to remove all mealy portions. The cleaned bran hulls are then mixed with hot water which is run off after settling and the prepared hulls put in the drench vat with the necessary water. The fells are first driven for 10 minutes in water of 25° C. to which a portion of the bran has been added and are then hauled, drained and put in the drench at 25-31°; they are driven with poles 15 minutes and the vat is then covered for 7-12 hours. When the fells float because of gas, mild ware is sufficiently bated, harder ware can be pressed down 1-2 times again. The completion of the drenching can be recognized by stretching the fell over the back of the hand, when the bran hulls adhering to the flesh should show through the grain; further the skin readily yields at the back and neck when pulled. The fells are then rinsed in the drench liquor, cleaned from bran with the grain iron and laid out dry from the beam for tawing.

The tawing paste ("Gar") which greatly varies, normally contains 4 kg. alum, 1 kg. salt, 12 kg. wheat flour, 140-150 egg yolks, 30 liters water. It is essential the flour be of the finest; the particles penetrate the fell, serving as filling and "nourishing" material and act on the alum during storage preventing spewing. Fresh egg yolk is the best but barrelled egg yolk is generally used on the large scale. One liter preserved egg-yolk = 50 yolks. The amount of alum must be exactly suited; when too much it deposits crystals in the grain, preventing a gloss and giving a harsh feel. With the sorting in equivalent lots as described at the outset, the computation is the same for all. The salt should never be more than ¼ the alum; with greater amounts the leather attracts moisture from the air and the gloss suffers. For one of the above lots, 12 kg. alum, etc., are used. For economy the tawing may be done in the drum, but for quality, treading by foot in the tub is employed. The leather loses firmness in the drum and becomes too loose. To prepare the paste for the tub, the flour is made up with warm water to a stiff porridge and then well trodden. The egg yolk is diluted with 10 liters luke warm water, sifted, added and trodden in. Then the alum and salt solutions of 56° C. are added and finally water so that the whole is at 40-44° C. All these additions are carefully made in portions, each being fully incorporated before the next is added. For treading, 5 men are required, the first stage being 30 minutes, then 10 minutes rest; 3 such turns are required when the paste should be entirely on the fells. They are let cool a few hours, then folded on the

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back grain to grain, and hung over poles to dry; when dry, they are turned to avoid creasing. This drying is at 37-50° C. at the highest in well ventilated rooms; 24-48 hours at the most. The dry hides are let shrink in a cool room and bound in packs. The currying is the same for all and will be described later. Kid leather will next follow.

(To be continued.)

PATENTS.

Process of Preparing Tanning Materials for Extraction. U. S. Patent No. 979,080. HERMANN MECHLENBURG, Köpenick, near Berlin, Germany, assignor to Nitritfabrik Actiengesellschaft.

The process consists in subjecting the material to the action of gaseous sulphur dioxide before leaching.

Leather Stripping and Trimming Machine. U. S. Patent No. 979,219. PETER STEIN, Chicago.

Apparatus for Making Extracts. U. S. Patent No. 979,362. WILHELM WIEGAND, Merseburg, Germany, assignor to Richard Rieder.

The material to be extracted is fed into one end of a long trough, along which it is pushed by a conveyor of the interrupted screw type. Water is introduced at the other end, where the spent material is removed. The liquor flows out of a high opening at end where the new material is introduced.

Belt-Stretching Device. U. S. Patent No. 980,490. GEORGE A. CLENDENNING, Mulberry, Indiana.

Leather-Working Machine. U. S. Patent No. 982,007. ALEXANDER H. KEHRHAHN, Frankfort-on-the-Main, Germany.

Leather Glazing Machine. U. S. Patent No. 982,398. WM. B. TURNER, Melrose, Mass, assignor to the Leather Finishing Machine Co., Boston.

Process of Making Sole-Leather. U. S. Patent No. 983,005. JOHN A. TANNER, Boston; LOUIS L. GREEN, administrator of estate of said tanner, deceased.

The process consists of partial tannage by the two-bath chrome method and then filling with vegetable tanning material.

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Journal of the

American Leather Chemists Association

Vol. VI APRIL, 1911 No. 4

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The opening meeting of this Congress will be held in Washington, D. C., Sept. 4, 1912, and subsequent sessions in New

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York City from Sept. 6th to Sept. 13th. A preliminary announcement has just been issued, which will be followed by other announcements as arrangements are completed.

In obedience to a joint resolution of Congress, President Taft extended through Ambassador Reid an invitation to the Seventh International Congress of Applied Chemistry to arrange for holding the Eighth Congress in the United States. The invitation was accepted and the thirteen delegates from the United States to the Seventh Congress were appointed as the nucleus of an Organizing Committee.

Twenty-four sections and subsections have already been organized, not as yet including a section or subsection on leather chemistry. The wish was expressed at the meeting of the American Leather Chemists Association in Chicago, October 1910, that our Association might participate as a Section in this Eighth International Congress. It is not too late for such an arrangement to be made. Members who wish to have our Association participate should urge the Council to take action to that effect.

ON THE COMPOSITION OF TANNING MATERIALS. I.

BIBLIOGRAPHY, 1828-1909.

By Dr. Arthur L. Dean, Sheffield Scientific School, Yale University.

The composition of the tannins, and the nature of the substances which accompany them in nature and appear to have some genetic relation with them, have been the subject of a very considerable number of scientific investigations. Some of these studies have been directed wholly to the problems of organic chemistry and had but remote relation to any practical applications; others have plainly had for their object the identification of tannins in mixtures or the possible equivalence of different tannins.

A practical problem of growing importance to leather chemists is the qualitative examination of tannins in extracts, and with the increasing use of extracts the significance of such examination becomes more evident. As a preliminary to studies directed to this specific practical problem a review of the past work bearing on the subject is indispensable, and as a first step

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in such a review the following bibliography is presented, covering the more important contributions up to the close of 1909.

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[1]Titles in parentheses are not exact titles, but indicate the character of the contents of the articles.

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ON THE USE OF OAK LEAVES IN TANNING.

By the Rev. Mr. Swayne.[1]

(In connection with Dr. Dean's bibliography printed in this number, readers of the Journal may be interested in this article, believed to be one of the very earliest on the subject of tanning chemistry. Mr. Swayne describes one of the first attempts to determine the quantity of tannin in a tanning material, and makes one of the earliest suggestions ever printed in regard to the manufacture of a tanning extract. One would have to consult a very old dictionary to find the meaning of "calx of iron" and "martial vitriol," but the context explains them sufficiently.—Ed.)

Knowing that the bark of the oak was a chief material in the art of tanning leather, and conceiving that every other part of that tree was fraught with the same astringent principle, through which the bark becomes so efficient in that art, the thought had often occurred that the leaves might be advantageously applied for the same purpose. Having in my possession a quantity of those leaves, which had been collected on account of the galls attached to them, I was desirous of ascertaining the proportion of astringent matter contained in them, and of comparing it with that contained in the bark. It was some time before I could think of a method of doing this, and whether the method I at length used was fully adequate to the intention must be left to the determination of those who have more knowledge in chemistry than I can pretend to. The well-known property which this astringent matter possesses, of uniting or striking a black color with the calx of iron, suggested to me that its quantity might probably be ascertained by extracting this matter through the medium of hot water, in which it is known to be soluble, saturating the extract with a known weight of the calx of iron, and afterward filtering, drying and weighing it. Supposing martial vitriol to contain iron in a very proper state for this experiment, the first thing I had to do was to ascertain the weight of iron in a given weight of vitriol, and this I attempted by the following process: I weighed five pennyweights of

[1] Published in the *Transactions* of the Society of Arts, Manufactures and Commerce in 1792 and copied into the *Literary and Biographical Magazine and British Review* for April, 1793, from which we take it.

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vitriol, dissolved it in water and added a like weight of vegetable fixed alkali, which immediately precipitated the iron. The mixture was then thrown on a paper filter, the weight of which was noted down, and after being plentifully elutriated with hot water, the residue was dried and weighed. Its weight, exclusive of the filter, was two pennyweights, thirteen grains. This proportion of iron in martial vitriol differs from that given by Professor Neumann from his analysis, but it is necessary to mention that the vitriol which I made use of had been kept in a dry place, uninclosed in a glass vessel, by which it had lost much of its water of crystallization, and this accounts for the difference. At the same time and from the same parcel of vitriol, I weighed several other portions for after experiments.

The weight of iron in a given weight of vitriol being known, I then attempted to follow the process above suggested; but upon trial found that the colored particles were so minute or so intimately mixed that they passed with the fluid through the filter. This I attributed to the presence of vitriolic acid, and its close attachment to the colored particles. With a view, therefore, to destroy this suspected combination by presenting to the acid a substance with which it has a nearer affinity, I added some mild salt of tartar, which instantly produced the desired effect, and brought on an entire separation of the colored mass. I then went on with my intended experiments in the following manner.

I took a half-peck measure full of dried oak leaves well pressed down, from which I had before separated several ounces of mushroom galls, and having put them in a brass kettle with a sufficient quantity of water, boiled them therein for two hours. The decoction was then poured from the leaves and fresh water added to them. This was likewise boiled for a considerable time, till it was judged that the water had extracted all the astringent matter. Both decoctions were then boiled down in the same kettle to one gallon. In a certain measure of this concentrated extract, I dissolved five pennyweights of green vitriol, and afterward added the like weight of salt of tartar. This mixture was then thrown on a filter of sinking paper, the weight of which was three pennyweights, and after being perfectly elixated with hot water, the residuum was dried and weighed.

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	Dwts.	Grs.
Filter and contents	6	14
Filter	3	0
	3	14
Calx of iron	2	13
There remains astringent matter	1	1

Two pints of this reduced extract were still farther evaporated to one pint, and a like measure of this was treated as the former, giving 1 dwt. 21 grs. of astringent matter.

I then obtained from a tanner two pounds of oak bark, which was perfectly dry, and after cutting it into thin shavings with a plane, boiled it in three portions of water for several hours, till from the color as well as the taste of the last decoction the astringency seemed to be perfectly extracted. These several decoctions were added together and evaporated to the same quantity as those of the leaves, namely one gallon. An equal measure of this as above produced by the like treatment 2 dwts. 2 grs. of astringent matter.

A quart of this extract was further concentrated to a pint, and an equal measure of this was treated as before, the remainder of astringent matter being 4 dwts. 8 grs.

These experiments do not exactly tally, since in both with the leaves and bark, the amount of astringent matter in the second experiment ought to have been double that of the first. The supposition of a small inaccuracy in the weighing, or a small loss in the process of these experiments, will tend to reconcile them. Where the error lay in the first instance, I cannot pretend to guess. In the first experiment with the bark, the filter caught fire while it was drying, and although it was extinguished almost immediately, yet there must have been a loss of some grains from it. Notwithstanding the experiments do not perfectly accord, yet I think we may fairly deduce from them, provided the method of trial be not objected to, that half a peck of leaves contain nearly as much astringent matter as one pound of bark.

Oak bark was sold in this neighborhood last season for five guineas a ton. In its marketable state it is by no means sufficiently dry for preservation, and the tanners are obliged to dry it more perfectly, and at considerable trouble and expense they

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likewise get it cleaned from much extraneous matter. The loss of weight from these operations cannot, I should suppose, be estimated at less than twenty shillings per ton. What I mean is that if a ton of bark cost the tanner in the first purchase five guineas, the same weight of bark when properly dried and cleaned will stand him in six pounds five shillings; for the sake of easier calculation we will say six pounds. I have heretofore had oak leaves collected for the purpose of making hotbeds for melons (for which they are excellent), at three-pence and four-pence per sack of four bushels, or thirty-two half-pecks, which according to the conclusions above are equal to thirty-two pounds of bark, which at six pounds per ton comes to 1 shilling and eight-pence halfpenny and a fraction. If then my premises stand unimpeached, it will follow that the tanner might obtain as much astringent matter in leaves for four-pence as costs him in bark five times that sum. Whether it would equally answer his purpose remains to be proved.

There would undoubtedly be much trouble and some expense in drying the leaves, which would be necessary in order to preserve them, and they would occupy much room. Perhaps for these reasons the most economical plan would be to obtain a concentrated extract from them, on or near the place where they could be collected, which might be conveyed and stored in casks. This likewise remains as the subject of experiment, but before leaves can in any way be legally used by the tanner, it is necessary that the act of parliament be repealed which confines him to the use of ash and oak bark. This restriction was probably laid, not solely from the belief that those substances were the most proper for the purpose of tanning leather, but likewise, to encourage the planting and nurturing of those valuable timber trees. Be this as it may, at present it rather operates to their destruction, than to their preservation or increase, since the high price which oak bark now bears proves an irresistible temptation with needy proprietors to cut down their oaks before they arrive at a proper age for timber. Should oak leaves ever come in much request for tanning, this doubtless would prove an antidote to the rage of felling, and an effectual preservative of timber, since no one

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surely would ever think of felling his oaks prematurely whilst they yielded him an annual profit by standing.

N. B. The vitriol was in every case sufficient to saturate the astringent matter, and the quantity of salt of tartar sufficient for the acid.

THE LEATHER CHEMIST OF 1951.[1]

Prof. H. R. Procter.

Few of us remember much of the leather chemist of 1871, partly on account of our age-limit, but mainly because he did not exist! Men there were (all honor to them) like Jackson Schultz in America, and W. Nelson Evans in England, who devoted thought to the study of tanning, and freely gave to the public the results of their labor; and chemists like the late Prof. Knapp who threw valuable light on the theory of the process; but the properly trained chemist who makes the technology of leather his profession was not yet evolved. Those of us whose recollections enable us to judge of the advance which has been made since then, feel that it is a source of pride and encouragement; and knowing the accelerating ratio with which knowledge grows, look forward with curiosity and confidence to a time which only the younger of us will live to see.

To look forward 40 years may indeed be futile, for 10 may carry us beyond the limits which we can at present guess; but it may not be uninteresting to speculate on the road to be travelled by the young and vigorous men who will follow us. Prior to 1871, leather manufacture had indeed made great progress, but principally in mechanical improvements:—today and in the immediate future, it is, I believe, the turn of the chemist. During the last 20 years he has done much in sharpening his tools:—tannin analysis has been brought almost as near perfection as our present empirical methods are likely to carry us, and further progress can only be made through a much extended knowledge of the chemistry of the individual tannins, which is the more imperative since the advent of extracts has made adulteration and mixture so easy. Long before 1951 the

[1] From the *Shoe and Leather Reporter* of March 16, 1911.

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chemist will no doubt know the causes of the difference of one tannin from another and will very probably be able to transform and modify them at will, while their economical synthetic production is not impossible; but from their cheapness and abundance in the vegetable world it is at present more likely that they will prove the raw materials for new products. If this is to be done the chemist will have to be versed in the structural formulæ, and the general organic reactions, which at present he is inclined to regard as purely academic.

Apart from tannins, the general methods of analysis and control have been vastly improved, and will go on improving as the need for them becomes obvious. In my own Institute we have a small laboratory in the midst of the tannery, which is devoted to continuous control of limes and liquors, and all the other products which form part of the tanning routine; and we are continually finding new directions in which such control can be applied, and new methods of carrying it out. To develop this work, the future chemist must have a wide experience in the art of chemical analysis, and sufficient general knowledge of reactions, organic and inorganic, to invent new methods for new purposes:—the man who shirks his general analytical work because "it has nothing to do with tanning" will not be the chemist of the future, though he may be his bottle-washer!

Another branch which is usually considered at present superfluous, but which will be an important part of the equipment of the future leather chemist is that of physical chemistry, theoretical and practical, and especially of its modern sub-branch, the chemistry of colloids. To the present-day tanner the very names are repellant, and the idea of measuring electrical conductivities and potentials as an aid to leather manufacture will seem absurd; and I can only assure him that such means are actually in use, not only here, but in one of the most important light leather tanneries of Great Britain with very valuable practical results; and that in this particular direction we are still at the very beginning. To give some instances, the electrometric measurement of the potential of a hydrogen electrode is the only known way of measuring the actual acidity of a tan-liquor as it exists in the vat, which often has no direct relation to that

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determined by titration, but which is the only value which really measures the action of the acid on the hides. As this becomes understood we shall be able easily to control it as we wish, and to decide exactly how much or how little the hides shall swell in liming, drenching, or tanning. I may instance the fact that we are in this institute "neutralizing" our chrome stock with a liquid of Dr. Stiasny's invention, which goes exactly far enough, and will go no further if the goods are left in it a week, so that the process, (and the subsequent fat-liquoring) has completely lost its difficulties.

Possibly the future chemist will need to be an expert bacteriologist, but this is less certain, since in 1951 no one will be using dog or pigeon dungs, or bran drenches, and you will sterilize your hides and liquors, and add the required acid by measure. Very possibly by that date there will be no more vegetable tanning, since all the forests may have been converted into newspapers, and it may be necessary to print the *Shoe and Leather Reporter* on thin aluminum foil! It is probable, however, that the aluminium salts may be no longer needed for tanning, and even chrome may have to take a back place before some new tanning agent which we have not yet even considered.

This is a strenuous age, and there is prospect of a busy and useful life for the coming young man; but it would be well for the tanners also to lay to heart the fact that his education will be no less costly, and the needed knowledge no less than that of the physician; and that his pay and social status will have to correspond. Looked at from the public point of view, it is much more important to save the life of an industry than that of a millionaire, though we can hardly expect the latter to hold our opinion!

ABSTRACTS.

Enzymatic Studies. S. P. L. SORENSEN. (Continued).—The three curves relating to mixtures of sodium hydroxide (glycocol + NaOH, citrate + NaOH and borate + NaOH) have a point of inflection at ordinate 5, corresponding to 5 cc. NaOH and 5 cc. respectively of glycocol, citrate or borate. Below the ordinate 5, the three curves (corresponding to mixtures richer in NaOH) approach closely and soon coincide. This shows that in these solutions the

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concentration of hydroxyl ions is so great that the hydrolysis of the sodium salts of glycocol, citric acid and boric acid has been suppressed, or nearly so. Under these conditions the sodium salts (the glycocol salt containing one atom of sodium per molecule, the citric acid salt three, and the boric acid salt one) behave like other normal sodium salts not hydrolyzed, (*e.g.* sodium chloride), and the concentration of hydroxyl ions of the solution is determined almost exclusively by the excess of NaOH, taking due account of the incomplete dissociation of this hydroxide occasioned by the sodium salts present.

Table 7 shows the concentration of hydroxyl and hydrogen ions calculated for some mixtures of N/10 NaOH and N/10 NaCl (or other sodium salt not decomposable by hydrolysis). The degree of dissociation in each case is taken as 0.841, (see page 149). The last two columns of the table give the exponent of hydrogen ions calculated for these so-

TABLE 7.

COMPARISON BETWEEN MIXTURES OF THE SODIUM SALT OF GLYCOCOL AND NaOH ON THE ONE HAND, AND ON THE OTHER, MIXTURES OF SODIUM CHLORIDE AND NaOH.

Composition of the mixture of glycocol	Alkalinity alk.	For the mixtures corresponding to N/10 NaCl and N/10 NaOH, there have been calculated: Concent. of hydroxyl ions alk.$\times$ 0.841 $= 10 - q$	Exponent of hydrogen ions $14.14 - q = p^1$	Exponent of hydrogen found by experiment for the mixture of glycocol p
		q	p^1	
0 cc. glycocol + 10 cc. NaOH ..	0.1 norm.	1.075	13.065	13.066
1 cc. glycocol + 9 cc. NaOH (= sodium glycocollate + 8 cc. NaOH).....	0.08	1.172	12.968	12.972
2 cc. glycocol + 8 cc. NaOH (= sodium glycocollate + 6 cc. NaOH).....	0.06	1.297	12.843	12.856
3 cc. glycocol + 7 cc. NaOH (= sodium glycocollate + 4 cc. NaOH).....	0.04	1.474	12.666	12.674
4 cc. glycocol + 6 cc. NaOH (= sodium glycocollate + 2 cc. NaOH).....	0.02	1.775	12.365	12.399
4.5 cc. glycocol + 5.5 cc. NaOH (= sodium glycocollate + 1 cc. NaOH).....	0.01	2.075	12.065	12.095
4.9 cc. glycocol + 5.1 cc. NaOH (= sodium glycocollate + 0.2 cc. NaOH)	0.002	2.775	11.365	11.565
5 cc. glycocol + 5 cc. NaOH (= sodium glycocollate + 0 cc. NaOH).....	0.0	7.070	7.070	11.305

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lutions (p') and the exponent of hydrogen ions found by experiment for the corresponding mixtures of glycocol, (p).

The concordance between the values p' and p shows that mixtures of glycocol containing any considerable excess of NaOH are to be considered essentially as solutions containing sodium hydroxide and a normal non-hydrolyzable sodium salt.

That the hydrolysis has not been entirely suppressed is shown by the fact that in every case p is a little higher than p', which certainly cannot be attributed to experimental errors. It is only when the mixtures contain a very small excess of sodium hydroxide that the hydrolysis of the glycocol goes further.

There is no well defined point of inflection on the glycocol hydrochloric acid curve at the point 5 cc. HCl + 5 cc. glycocol, which may be accounted for by the fact that the acid character of glycocol is more strongly marked than its power to form a definite compound with HCl.

The other branch of the curve of citrates presents a well marked point of inflection at the mixture 3.33 cc. of citrate + 6.67 cc. HCl, (corresponding to free citric acid), and also the curve of borates shows a manifest point of inflection at the mixture 5 cc. of borate + 5 cc. HCl, the point at which boric acid begins to be liberated. For mixtures of borates richer in HCl, boric acid has no importance in regard to the hydrion concentration, which is determined solely by the excess of HCl, taking into account the sodium chloride present.

REASONS WHICH LED TO THE SELECTION OF THE STANDARD SOLUTIONS EMPLOYED.

The important part taken in proteolysis by the content of phosphates has already been shown in a research carried out by Fr. Weis in the Carlsberg Laboratory and published in 1902,[1] on the proteolytic enzymes of malt. Weis confirmed the results of A. Fernbach and L. Hubert[2] that the proteolytic power of a malt extract increases with the addition of acid, until all of the secondary phosphate has been converted into the primary salt, but that the further addition of acid diminishes the enzymatic power. The addition of base, however, hinders the proteolysis, the hindrance being greater as the amount added is increased. This effect is especially marked if the alkali added is more than enough to convert all the primary phosphate into secondary.

A series of experiments in the Carlsberg Laboratory by Messrs. Petersen and Sollied in 1902 and 1903 on the enzyme of yeast, also showed that the quantity of primary and secondary phosphates in the medium has an important influence on the speed of proteolysis.

More recently Fernbach has shown that the solvent action of diastase on starch depends among other things on the presence of phosphates,

[1]Comptes rendus, 5, 216.

[2]Comptes rendus, 131, 293, (1900).

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the primary favoring the reaction and the secondary tending to prevent it.

It seems scarcely likely that the primary or secondary salts as such can hasten or retard an enzymatic reaction, so we may explain their action by supposing that the concentration of hydrogen or hydroxyl ions in the medium is determined by the ratio of primary and secondary phosphates present. If a small quantity of acid or base be added to such a mixture of phosphates, the only effect is to convert a part of the secondary salt into primary, or the reverse. The hydrion concentration in the solution suffers no change beyond that due to the altered proportions of the two phosphates. Such a mixture of phosphates affords, then, a natural protection against too sudden changes in the hydrion concentration: The mixture serves as a "buffer" ("tampon"). (See page 137, March number of the JOURNAL.)

Mixtures of normal carbonates with acids, as also acid carbonates containing an excess of CO_2 may also serve as buffers, as they often do in nature. A 1/20 molecular solution of normal sodium carbonate has a hydrion concentration corresponding to the index 11.39, while the index of a 1/10 molecular solution of sodium bicarbonate is 8.40, and of this same solution saturated with CO_2, 6.8 to 6.9. As may be seen by a glance at the chart of curves (in the March number), a solution of sodium carbonate containing CO_2 may serve as a buffer over a range of ionic concentrations similar to that covered by the mixtures of phosphates.

In the case of pepsic digestion the optimum hydrion concentration is entirely outside of the range here considered, so that neither phosphates nor carbonates can be used as a regulator in this reaction. In pepsic digestion the buffer is the process of molecular splitting itself, since protein and its decomposition products are capable of fixing both acids and bases.

In selecting liquids of comparison having hydrion concentrations comparable to those which play a part in enzymatic splitting, everything seems to indicate that it will be well to use such substances as serve for buffers in natural processes.

The first liquors of comparison used by the author were mixtures of phosphates and of glycocol. Glycocol was chosen as representing proteids and their decomposition products because it has a simple composition and is easily procured. It will be noticed on the chart of curves, that the curve of phosphates covers the range in which the glycocol curve is useless. It appears that other products of proteolysis as well as the proteids themselves behave essentially like glycocol. In consequence, neutral solutions of these substances to which small quantities of acid or base have been added, deviate much at the neutral point ($p_H^+ = 7.07$), at least if these solutions do not contain phosphates or carbonates capable of acting as buffers.

Examining the chart of curves further, it is evident that while it

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is possible by means of mixtures of phosphates and glycocol to prepare liquids of comparison for all ranges of ionic concentration from N/10 HCl to N/10 NaOH, yet in consequence of the form of the curves, from the point where the curve of phosphates ceases to that where the curve of glycocol (with HCl and NaOH respectively) begins, there are ranges of concentration where there is need of other standard solutions. As the chart shows, this need is especially felt in one of these regions, that in the neighborhood of $p_H = 4$, and this is precisely the region of chief interest in the case of many enzymatic reactions. It was therefore necessary to supplement the phosphate and glycocol mixtures with new standard solutions. For this purpose the mixtures of citrates and borates already described were chosen, and served very well.

PARTICULAR CASES WHERE ELECTROMETRIC MEASUREMENTS ARE DIFFICULT.

Even if we employ the apparatus described, and are sure that the hydrogen electrode is working properly, there are yet cases where a precise electrometric measurement is difficult to make, either because the liquid being examined changes of itself during the measurement, or is modified by the action of the platinum electrode. Four cases are discussed.

First. Liquids containing carbon dioxide or carbonates cannot ordinarily be measured electrometrically with sufficient precision, except in cases where the liquid is so acid that all the CO_2 is free and can be expelled by a current of hydrogen, without sensible modification of the hydrion concentration, and in the opposite case where the liquid is so strongly alkaline that no CO_2 is carried out by the current of hydrogen.

A 1/20 molecular solution of normal sodium carbonate may be exactly measured by the electrometric method, but not a 1/10 molecular solution of sodium bicarbonate. A colorimetric measurement of the latter gave $p_H^+ = 8.4$, while an electrometric measurement gave the results which follow. The current of hydrogen was started at 11 o'clock, and π was observed to increase. Exact readings were taken beginning at 11.08, as follows:—

Hour	π	p_H^+
11.08	0.8120	8.22
11.11	0.8218	8.39
11.17	0.8283	8.50
11.30	0.8341	8.60
12.30	0.8475	8.84
1.30	0.8543	8.95
2.30	0.8591	9.04
4.30	0.8682	9.19

These figures show clearly that it is not possible to determine by this

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method the hydrion concentration of a solution of this sort, for it would be quite arbitrary to choose the value of $p_H^+ = 8.39$ (after 11 minutes flow of hydrogen), a value which agrees with that found by the colorimetric method. One ought rather to choose the higher value $p_H^+ = 8.60$, because in electrometric measurements constant values of π are commonly obtained after a half hour's flow of hydrogen. By making a colorimetric measurement after the close of the electrometric tests, it was shown that the changes in the value of π were caused by a real change in the hydrion concentration of the solution, and not by a poisoning, so to speak, of the electrode. The value obtained was $p_H^+ = 9.13$, using glycocol mixtures as liquids of comparison, and phenolphthalein as indicator. Solutions liable to give rise to errors of this kind were prepared a day in advance, and hydrogen run through them over night to drive out the CO_2. Both electrometric and colorimetric measurements were then made and the results compared. In the case of sea-water the small percentage of CO_2 was expelled by a current of hydrogen. The hydrion concentration was then measured by both methods, in order to determine the degree of accuracy obtainable by the colorimetric method. These measurements could not be taken as final because the hydrion concentration might have been altered by the passage of the hydrogen. The original liquid was therefore measured colorimetrically, (it being assumed that the accuracy of this method is not affected by the presence of CO_2), and the result corrected if necessary by means of the comparison already made.

This method cannot be employed in the case of some physiological liquids containing CO_2. Blood is an example. It cannot be treated colorimetrically. Protoplasm and serum are other cases, and here the difficulty is that no indicators have been found which are capable of exact results in the case of liquids with a high content of natural proteids. In such instances a slightly modified electrometric method is used. The electrolytic vessel is filled with the liquor to be examined and hermetically sealed. Then a quantity of hydrogen is introduced sufficient to cause the level of the liquid to fall to a certain point, so that a part of the electrode is surrounded by hydrogen. In this way no considerable loss of CO_2 takes place, but ordinarily the electromotive force does not become constant until after a relatively long time (6 to 8 hours, or even more).[1]

Second. In the case of a solution whose ionic concentration is not stable, it is evidently impossible to make direct electrometric measurements. After passing H for half an hour, dependable readings may be made, and if a series of measurements follow, the rate of

[1]According to Carlo Foa (Archivio di Fisiologia, 3, 383, (1906), this is not the case with platinized gold electrodes, and still less with palladium, which rapidly come to constant potential.

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change of ionic concentration in the liquid may be determined. If now a curve be made with the measured values, this curve may be extended backward to the time when the solution was mixed.

Third. Influence of toluene or chloroform. In enzymatic researches it is customary to use toluene, chloroform or other antiseptics to prevent the growth of bacteria in the solutions. In measuring such solutions, especially when the gas electrode is freshly prepared, difficulties are encountered, the most notable being that the *e.m.f.* does not at once become constant. Freshly coated electrodes are much influenced by either toluene or chloroform, more strongly in acid than in alkaline solutions. After being used several times, however, the electrode gradually loses this sensitiveness; immunizes itself, so to speak, against these substances. Electrodes thus immunized give nearly accurate results, especially if the quantity of toluene admitted to the apparatus be very small, so that it may be quickly eliminated by the current of H.

Because the toluene introduces a small uncertainty, and because even a large growth of mold in the standard solutions makes no measurable difference in their hydrion concentration, the author has abandoned the use of toluene, and the observations tabulated on pages 151 to 154 were made without it.

Fourth. When the solution to be examined is subjected to the action of hydrogen in contact with platinum sponge, it is evidently possible that the hydrion concentration of the solution may be changed, and that in consequence the electrometric method may become uncertain or even inapplicable. The case is further complicated when the hydrogenization of the solution gives rise to substances which exert an injurious effect on the electrode. An instance of this is found in some experiments on egg albumen, treated with NaOH and then acidulated with HCl. The platinum electrode was at once strongly affected by this solution, which smelled slightly of hydrogen sulphide. Even after the expulsion of the gas by a current of air or hydrogen, the liquid under the combined action of the hydrogen and the platinum electrode, but not in the absence of the latter, continued to evolve small quantities of H_2S, and to exert an appreciable influence on the electrode.

(To be continued.) L. B.

The Drying of Leather. *Gerber-Courier*, **51**, (1911), No. 6, p. 1.— Drying is a very important part of the tanning process. If the water has contained any objectionable matter, such as iron, saltpeter or chalk, these will show on the dried leather. A drying room must above all things be clean, for dust shows on the hides. It is unnecessary to have the drying rooms low, for since the hides are hung on the ceiling they get the warmth no matter how high the ceiling is. The damp air developed by the drying hides should be drawn off by some practical method, such as ventilators or exhaust fans. By this method the ventilator forces warm air from a separate room into the drying

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room, whence it escapes out of doors, thus keeping up a circulation and drying the hides very quickly.

Another method which is cheaper is by means of draft boxes placed at intervals around the floor. In this case the room is usually heated by steam pipes at intervals up the walls, and the heavy damp air settles to the bottom, escaping through the flues. These must be warmed by pipes in winter or the air will not go out. Still another method is to place a turret on the roof through which the air escapes. The leather does not become perfectly dry by this method, which, however, does very well for sole-leather; but for skins which are to be glazed, all moisture must be removed. E. A. B.

Report of the Freiberg Research Institute for the Year 1910, by the Director, Prof. Dr. J. Paessler.—The total number of analyses made during the year was 5,640, three-fourths of which were of extracts and tanning materials. In the years 1908 and 1909 all analyses of tanning materials were conducted by both the filter and shake methods, but in 1910 most were done by but one, whichever the sender wished. In the table are given the average tannin content by each method for the samples examined in 1910 and the average difference for the samples of the last 3 years.

PER CENT. TANNIN.

	Filter method 1910	Shake method 1910	Difference 1908, 1909, 1910
Oak bark	11.5	10.6	0.8
Pine bark	12.6	10.9	1.8
Mimosa bark	32.8	29.7	1.5
Mangrove bark	39.9	39.7	1.5
Valonia	34.0	29.2	2.5
Trillo	44.5	40.8	3.0
Myrobalans	37.4	31.9	4.5
Myrobalans, hulled	50.9	47.4	6.0
Divi divi	46.6	37.8	4.0
Quebracho wood	20.8	19.9	1.0
Sumach	27.4	24.3	2.2

Various other substances yielding tannin were examined, including a few samples of oak and chestnut wood. Average results for these in soluble tannin were as follows:—

	Filter method	Shake method
Oak wood	11.3%	10.7%
Chestnut wood	11.0%	.....

The non-tans were much lower in the chestnut wood than in the oak, ranging from 1 to 3 per cent. in chestnut and from 4 to 8 per cent. in oak.

Many samples of tanning extracts were examined during the year. The results of these will be published in a forth-coming work on the sugar-content of various tanning materials and tanning extracts. Some

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of the oak-wood extracts showed a very high proportion of non-tans, the highest being 19.7 per cent. non-tans to 20.5 per cent. tannin.

Many chestnut wood extracts were examined, the figures for a few of which are given. The pasty extracts range from 41.9 per cent. tannin, 10.4 per cent. non-tans and 47 per cent. water to 44.7 per cent. tannin, 13.2 per cent. non-tans and 42 per cent. water. The solid extracts range from 73.5 per cent. tannin, 11 per cent. non-tans and 12.3 per cent. water to 55.9 per cent. tannin, 18.5 per cent. non-tans and 24.3 per cent. water.

1,279 samples were examined which came in as quebracho extract, liquid, pasty and solid. Many of these were not pure quebracho, containing myrobalans, mangrove and even molasses. A few instances are given, an extreme case showing 50.1 per cent. tannin, 30.2 per cent. non-tans and 19.1 per cent. water in a solid "quebracho." Solid quebracho regarded as genuine gave 64 per cent. tannin, 5 per cent. non-tans and 26 per cent. water to 77 per cent. tannin, 4 per cent. non-tans and 14.5 per cent. water, insolubles ranging from 0.2 per cent. to 7.3 per cent.

A few figures are given for pine bark extract, the best being 26.1 per cent. tannin, 13.3 per cent. non-tans, 0.7 per cent. insolubles and 59.9 per cent. water.

420 analyses were made of leather and leather articles. The highest content of water-solubles in a leather not "loaded" was 25.9 per cent., 21.8 per cent. of which was tannin. In the loaded leathers, as high as 2 per cent. of magnesia was found, corresponding to 12.3 per cent. crystallized magnesium sulphate. A sample of chrome leather contained 9.1 per cent. sugar, and 13.2 per cent. alkaline sulphates. Another chrome leather had 12.2 per cent. common salt, 10.9 per cent. barium chloride and 1.8 per cent. barium sulphate, a total load of 24.9 per cent. Several samples of brittle leather were found to contain a large amount of free sulphuric acid, in one case as high as 1.87 per cent. A leather with brittle grain contained in the surface layer a considerable quantity of oxalic acid.

A material sold as a deliming agent contained 5.8 per cent. sugar and 20.6 per cent. sulphuric acid. L. B.

Salts of Titanium as Dyeing Materials for Leather. *Le Cuir*, 4, 4, p. 113.—As compared with the salts of aluminum, iron, chromium and copper, titanium compounds are very stable, and therefore make excellent pigments. Titanium salts used as mordants form very durable "lakes" with dyes, and many of the titanium compounds themselves have serviceable colors and are used as dyes. Antimony salts have long been used to fix tannin on the fiber of leather, giving a natural tan color. Titanium salts, however, not only fix the tannin very firmly, but give a deep yellow color, and with the use of a small quantity of material.

Basic dyes cannot be employed at the same time with titanium salts, but acid dyes may be used with them to great advantage. If basic dyes are used, the titanium salt is added afterward, and good results are

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thus obtained. The quantity of titanium employed is about one-fourth per cent.

Titanium salts used as mordants with natural dyes such as fustic behave in the same way as with tannin, furnishing very fast colors. Campeachy wood with titanium makes a very good black. L. B.

Artificial Degras. *Chem.-Techn. Fabrikant* through *Ledertechn. Rundschau*, 1911, 34-5.—As a substitute for the genuine article, (the product of chamoisage) oxidized marine oils are emulsionized as follows: (1) 60 parts with 10 crude wool grease, 30 water; (2) 60 parts with 5 bone fat, 10 wool grease, 25 water; 30 parts with 20 wool fat, 20 ordinary whale oil, 20 water. 3-4 hours milling are required. To make the product still cheaper, mineral and rosin oils may be added; a more permanent emulsion is then secured by addition of alkali. An Austrian method consists in tanning hide offal, best with alum, then impregnating this with whale oil and piling the mass in a warm room. Oxidation is complete in 3-8 days; the oil is pressed out and the leather may be re-used. W. J. K.

The Analysis of Degras. W. FAHRION. *Collegium*, 1911, 53-7. I. *Determination of Water and Ash.*—Three grams degras are heated directly in an open platinum crucible until the foaming ceases and a sizzling begins with finally a slight smoking. With practice this end-point may be reached with a concordance of 0.2 per cent. The residue is ashed but for accurate work a charge of at least 50 grams is needed.

II. *Free Fatty Acids, Unsaponifiables, Total Acids and Oxy-acids.*—Three grams degras are weighed in a 100 cc. porcelain dish (outside matt) and titrated with N alkali, N/2 finish, to red (phenolphthalein); this is computed as oleic acid, mol. wt. 282. To the neutral solution 3 cc. 5 per cent. aqueous KOH are added and evaporated on the water-bath, finishing by direct heat cautiously to dryness. The soap is dissolved in 50 cc. 50 per cent. alcohol and extracted successively with 25 + 15 + 15 cc. petrol. ether, boiling below 70°. The united extracts are shaken with 20 cc. 50 per cent. alcohol which is finally added to the soap solution. The residue from evaporation of the petrol. ether extract = unsaponifiable. The alcohol soap solution is evaporated to dryness, the residue dissolved in hot water and when cold shaken well with 25 cc. petrol. ether and 10 cc. 20 per cent. HCl and let stand over night. The acid solution is drawn off and the petrol. ether layer on evaporation yields total fatty acids. The oxy-acids or "degras-former" remain in the funnel; these are dissolved in warm alcohol, evaporated to dryness and weighed, then ashed and again weighed; the difference = oxy-acids. A portion, however, remains in the acid solution and is recovered by evaporating, redissolving in a little alkali or NH_3, not over 10 cc. H_2O, then shaking as before with petrol. ether and HCl. The sum of water + ash + unsapon. + total fatty acids + oxy-acid = 95-96 per cent. of the degras; the difference can be reckoned as glycerine and loss.

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The water in degras is normally 15-20 per cent.; English sod oil has 30-40 per cent. Water-free sod oil is sold but from the long boiling is almost black. The ash is slight, 0.3 per cent. at the most; soap was formerly added but seldom now, Traces of Fe are generally present and harmless below 0.03-0.05 per cent.; at times, however, even the smaller amount may be troublesome, probably from precipitation as Fe soap. Marine oils contain mostly 1-2 per cent. unsaponifiable but this can reach 3 per cent. in cod and shark oils. On conversion into degras these ratios are not changed, but they naturally increase on addition of mineral oil or wool fat. Within limits such additions are useful and not adulterations; for instance, a highly oxidized degras will not penetrate leather without mixture with mineral oil. The content of total fatty acids is naturally higher, the lower the unsaponifiable and oxy-acids. The molecular weight determination by titration is not important; it averages 300. The saponification number of the original degras fluctuates according to the degree of reaction since the oxy-acids besides the COOH group also contain weaker acid groups. The iodine number, however, is of value in connection with the resinifying power. This evil feature shows when the oil has been insufficiently oxidized; if the iodine number is below 100 resinification need not be feared. The content of free acid varies much in oils, hence in degras itself. If it exceeds 20 per cent. (reckoned as oleic acid), spewing may result. This consists of a coating on the leather of saturated acids. Views differ as to the desirable amount of oxy-acids (degras-former); the percentage depends upon the iodine number of the original marine oil employed in manufacture and upon the degree of oxidation, 15 per cent. or more may be reached, but 6 to 10 per cent. is best for practical use. The oxy-acids in degras are not free, but present principally as glycerides, hence anhydrous degras is completely soluble in phenol ether. These glycerides are valuable and important in saturating leather after tannage and making it soft. The German degras manufacturers have mutually agreed to furnish two brands of degras:

Moellon, maximum 17 per cent. water, 6 per cent. unsaponifiable; moellon degras, maximum 20 per cent. water, 12 per cent. unsaponifiable. W. J. K.

A Pyknometer for Leather, Tanning Materials and other Solids. GEORG GRASSER. *Collegium*, 1911, 69-70.—Paessler determines the specific gravity of leather by measuring the mercury displaced by a strip of the material 25-30 cm. long, 1-1½ cm. wide. To read this with accuracy, the author has devised a special burette made by Arthur Meissner, Freiberg, Saxony. The weighed solid to be examined which may be in divided form if desired is contained in a displacement tube the stopper of which terminates in an elongated narrow tube bearing the zero point. The tube is connected below by rubber tubing with a narrow burette tube in which the mercury level is read before and after

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introduction of the sample. The mercury level is adjusted to zero in the displacement tube at each reading. W. J. K.

Notes on Tannin Solutions. GEORG GRASSER. *Collegium*, 1911, 46-52. —Iodine was first used by Jean for the determination of tannin in alkaline solution, the end-point being ascertained by an external spotting test on starched filter-paper. The author found that an excess of iodine was more easily detected by allowing the test liquid to flow into starch solution contained in a porcelain dish. He employed the method to determine gallic acid (abstract, JOURNAL, 5, 582). He now reports investigations upon the sensitiveness of the reaction for qualitative tests. The various tannin solutions were acidified with 20 per cent. H_2SO_4 and N/50 iodine added drop by drop until a test with starch paste gave a violet color. With solutions containing over 0.1 per cent. the starch could be added directly and iodine added with warming until the violet appeared on cooling the test. The limit of the reaction was found to be 0.001 per cent. of gallotannic acid which gave immediately a weak violet (external test).

Other reagents were compared; tartar emetic alone and with various admixtures was not very sensitive; ammoniacal zinc acetate still gave a slight opalescence with 0.0005 per cent.; gelatine-salt reagent seemed to be the most reliable for used liquors rich in non-tans. In testing various materials, pine was found to give a violet color with iodine alone without starch; the reaction was more decided after boiling.

Finally the author discusses the cause of "detannizing" of tannin solutions on standing. He prepared clear solutions of various materials, mixed these in all possible pairs and observed no clouding due to a mutual reaction. After standing 2 days only those mixtures containing quebracho or valonia gave a slight sediment. W. J. K.

Glove Leather Manufacture. (Conclusion.) *Ledertechn. Rundschau*, 1910, 410-11; 1911, 1-3, 9-10, 17-19, 26-28, 33-34.—*"Fasson" Kid Leather.*—Both lamb and kid fells may be worked and in the same way, the former with more caution. They are carefully sorted, rejecting all without a fresh bright grain as unsuited for this sort of leather, likewise those which held towards the light show streaks in the sides and flanks; these will not withstand the beam work. Ware which has been heated in drying or storage as evident by the dull grain and glued hair is discarded. The soaking must be finished in 2 days; spring water is best. With hard skins once used water may be employed the first day, then fresh water sharpened with 1 kg. caustic soda to the hectoliter. The liming should be complete in 10-12 days; a liquor should not be used over 4 weeks. A series of 5 pits is best. For 600 large (800 medium, 1,000 small) kid fells, 14 hectoliters liquor are needed. The charges for such a lot are 60 liters stiff slaked lime, 1 kg. red arsenic, distributed in the 5 pits so that at each shift 20 l. lime, 550 gm. arsenic go to the fresh liquor, 16 l. lime, 450 g. arsenic to the next best, and to the others 12, 8 and 4 l. lime alone. After liming, the fells are carefully rinsed

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and left over night in clean water. The unhairing is done on an elastic beam with a well polished iron, care being taken in scraping away the scud that this be not pressed in and permanently fixed for which there is no remedy. After the beam work (Fassons) which is minutely detailed comes a bran bate at 34-35° C. The tawing is also as with lamb-fells, the proportion of flour and egg being increased; 40 kg. flour, 500 egg yolks, 8 kg. alum, 2 kg. salt, 100 l. water to 600 large fells.

Currying.—The dry fells in packs of 50-100 are dipped in water, untied, covered with cloths and left in the bin 24-36 hours. They are trodden by laborers at intervals for 3-4 days and are ready for the principal operation, moist staking, which must be done very evenly. After partial drying, the fells are again left over night under cover, then smoothed, packed in lots of 10-12 and sent to the white storage (Weisslager). The storeroom should be dry and well ventilated as this leather is extraordinarily hygroscopic and moisture must be guarded against. The leather is stored at least 4 weeks before further treatment.

Flesh Leather ("Chairleder").—This requires denseness and a smooth velvety flesh. Lean or coarse fibered fells are unsuited and cannot be pumiced. The soaking must be quick with water sharpened by sulphide or better caustic; old soaks are excluded. In liming, lime is kept down to the minimum, sulphide being the chief agent. A new liquor is prepared with 15 l. lime paste, 1,800 gm. sod. sulphide to a cubic meter. Five pits are used, shifts every 2 days. For bettering, 10 l. lime paste, 1,440 gm. sulphide are used for the best pit, for the next 5 l. lime, 1,080 gm. sulphide, for the next 720 gm. sulphide only, and the oldest, nothing.

Sulphide is best added from a stock solution of 6 kg. to 100 l. The liming lasts 11-12 days. In dehairing, the fells are drummed with warm water, then washed at 22° C. After sorting and trimming, fleshing and bran bating, the tawing paste is applied as with glacé; 36 kg. flour, 50 egg yolks, 9 kg. alum, 2¼ kg. salt, 90 l. water to 1,000 medium fells.

Mocha Leather.—This is similar to the above, but is curried on the grain which is ground off to give the plush effect. For dehairing, a paste (Schwödebrei) is used; 1 kg. sod. sulphide in 53 l. water and 35 l. lime paste, all to 100 l.; this is applied for 12-14 hours. After unhairing, the fells are given a straight lime for 6-8 days. After shaving, they are delimed with HCl, washed and scudded. Alum alone is used for the first tawing, 2 kg. alum, 200 g. calcined soda, 500 gm. salt to 100 medium fells, trod in warm at 31°. Finally the grain is half removed by polishing with emery and the leather is then again tawed with alum and egg.

Dyeing.—The demands of the trade are much more stringent than formerly; the color must be precise in tone and very uniformly applied. Two methods of dyeing are used: (1) the dip method, coloring

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the leather on both sides, used only for light shades since the flesh side takes up dye much faster than the grain; (2) the table method, where the grain only is dyed after applying a ground. For dyeing, pure water free from organic matter is essential; soft water is better than hard. If much lime be present, this is precipitated in the ground, roughening the grain, hindering or preventing dyeing. Careful sorting of the fells is needful; fine grain, thin fells are selected for thin leather and dip dyes. Before dyeing the sorted fells are subjected to the "broschiren" process; this consists in working the leather in water at 30 to 40° according to age until the particles of flour are completely removed from the grain and alum and salt can no longer be detected by taste. Treading gives the best results although the drum is cheaper. After draining, the fells are ready for the dye bath; for table dyeing, each skin first receives a "nourishment" of ½ to 1 egg yolk.

For the dip dye bath, the liquors are always fresh made, a short extraction of the wood or berries being sufficient. The liquor is to be filtered, even when aniline dyes are used. A series of 3, better 4 or 5 vats is used. If the drum be employed, the leather is put in motion with water at 37° and the dye added in 4 to 5 portions at intervals of 10-15 minutes, exhausting the dye each time. The dye may also be trodden in the tub, finally treating the leather with ½ to 1 egg yolk per skin and sufficient water. The drying is finished in 2 hours at 37° C. at the highest. The suspended fells are reversed once in the meantime to insure even coloring. The drying air should be warm but contain no fuel gas. Before staking, the leather is first layered on the flesh with moist sawdust, grain to grain pairwise in a box. Staking, trimming and grain polishing complete the process.

For straw yellow a decoction of wold is used, Brazil wood being added for rose shades; for sea green, privet berries; for flesh color (chamois), beginning with wold then Brazil wood, finally zinc vitriol; for rose, Brazil wood; lilac, elderberry and logwood; mauve, buckthorn-berries; apricot, Persian berries and Brazil wood. More brilliant tones are obtained by combining these various dyes with coal tar colors.

Table Dyeing.—This is carried out on a table covered with lead; the edges are upturned and the surface slopes towards the back for draining. Concentrated dye liquors are used; for black, 40 kg. logwood, 12 kg. fiset, 6.5 kg. fustic, 1¼ kg. soda, 1½ kg. ammonia are boiled with water 2 hours and made up to 500 l.; for blue 50 kg. Domingo logwood, 250 l.; for yellow, 50 kg. fustic, 250 l.; for red 50 kg. Brazil wood, 1½ kg. soda, 250 l.; for brown, 80 kg. fustic, 1 kg. soda, 250 l. It is easier to employ extracts which give more uniform solutions. The fell is smoothed moist and flat upon the table and first brushed with ground which the grain requires before being susceptible to most dyes. For this, human urine is the best medium; for light shades it is diluted with an equal quantity of water containing 1 per cent. borax. The dye is applied with two

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brushings, rubbed in, rinsed off and the fell slicked. After a third brushing, a mordant is applied containing in 200 l. 2 kg. green vitriol for black, 1 kg. Salzburg vitriol (iron and copper sulphate mixture) for dark colors, 1 kg. blue vitriol for middle tones, 2½ kg. zinc vitriol for bright red, 5 kg. alum for bright yellow. After drying, the leather is packed in the chest, grain to grain, with moist sawdust on the flesh. When sufficiently moist, it is staked and finally polished on the grain with a roller.

"Chairleder" before dyeing is sorted into fells of the heavier sort which are to have the grain removed and those which are not fitted for this such as the thinner, milder sort. The grain is removed with the paring knife. The next operation is the slicking which can be done by hand with the moon-knife but requires skill. On the large scale emery wheels are used to remove the flesh. After the "broschiren" in the usual way, the flesh is finally ground down on revolving stones of the proper hardness. The dye solutions are prepared rapidly; 15 minutes boiling is sufficient. Alum is used for mordanting. The dye is trodden in from the tub, being added in 5 or 6 portions; finally a "gar" of egg yolk is applied, a third or half that used for glacé leather. W. J. K.

Mangrove Tannin and its Decolorization. ADOLF ROMER. *Ledertechn. Rundschau,* 1911, 26-27.—The varieties of mangrove differ greatly in tannin content. The author quotes analyses of the seven principal varieties occurring in East Africa, ranging from 4 to 52 per cent. tannin. The three richest are Brugiera gymnorhiza, Rhizopera mucronata and Ceriops Candollona, and their tannin content increases with age. The objectionable red color of mangrove has prevented any considerable use of the material in Europe. The author together with Dr. Bosch have successfully solved the problem of bleaching the dyestuff without loss of tannin, the reducing agent being a small amount of chromous acetate. The process is the property of the German Colonial Tannin and Dyestuff Company of Feuerbach-Stuttgart and is patented in all countries. W. J. K.

PATENTS.

Multiple Effect Evaporating Apparatus. U. S. Patent No. 984,226. SAMUEL M. LILLIE, Philadelphia, Pa.

Evaporating Apparatus. U. S. Patent No. 984,754. F. H. EYDMAN, Ryswyk, Netherlands.

Method of Evaporating Solutions. U. S. Patent No. 984,822. SAMUEL M. LILLIE, Philadelphia, Pa.

Leather Skiving Machine. U. S. Patent No. 985,401. F. M. COURSER, Haverhill, Mass., assignor to United Shoe Machinery Co.

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Method of Setting Out Leather. U. S. Patent No. 985,466. JAMES T. SMITH, Newark, N. J.

Sectional Work-Support for Leather-Working Machines. U. S. Patent No. 986,497. FRANKLIN J. PERKINS, Woburn, Mass., assignor to Holder-Perkins Company.

Manufacture of Fatty Acids. U. S. Patent No. 987,426. GRACOMO BOTTARO, Genoa, Italy.

A current of steam, air and sulphur dioxide is passed through a lime soap, decomposing it into fatty acid and calcium sulphate.

Apparatus for Color Estimation. U. S. Patent No. 987,148. J. W. LOVIBOND, Salisbury, England.

An improvement on the well-known Lovibond tritometer.

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Journal of the

American Leather Chemists Association

Vol. VI MAY, 1911 No. 5

W. K. ALSOP . . . . . Editor and Manager
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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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[CONTRIBUTION FROM THE LEATHER AND PAPER LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

EXTRACTION OF LEATHER WITH 95 PER CENT. ALCOHOL.

J. S. Rogers.

Mr. G. A. Riker (this Journal, Vol. 5, No. 12, p. 539) describes a method for the extraction of leather, using 95 per cent. alcohol. It stated that the alcohol does not remove the sugars and Epsom salts and consequently avoids the misleading results

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obtained when Epsom salts are calculated in the water-soluble and again reckoned in the mineral ash; and also the error in the determination of uncombined tannins, due to the partial absorption of the sugars and Epsom salts by the hide powder.[1]

It is a well-known fact that sugars are purified by recrystallization from boiling alcohol (80-100 per cent.). According to Seidell (Dictionary of Solubilities) 100 grams of 85 per cent. alcohol dissolves 1.95 grams of dextrose at 17.5° C. Trey, (Die Chemie der Zuckerarten 1, 1904, p. 267) found that: 100 cc. of absolute alcohol, boiling temperature, dissolves 1.42 gm. of grape sugar.

Two samples of leather which had previously been analyzed in this laboratory were extracted, following in detail the method given by Riker. Sugars were determined by the usual method in the extract. The sample which gave, by the water extraction, 10.19 per cent. sugar gave 4.32 per cent. by extraction by 95 per cent. alcohol. The second sample which gave by water extraction 12.01 per cent. gave 3.20 per cent. sugar by extraction with 95 per cent. alcohol.

This shows clearly that the sugars are removed to an appreciable extent by 95 per cent. alcohol. In the two cases above, between 25 per cent. and 40 per cent. of the sugars present being extracted.

Comey (Dictionary of Solubilities) states that 100 parts of absolute alcohol will dissolve 1.3 parts of $MgSO_4.7H_2O$ at 3° C. In this laboratory 5 gm. of Epsom salts placed in an S and S thimble and extracted in a Soxhlet extractor for two hours (approximately 12 siphonings) with 95 per cent. alcohol, gave 0.0121 gm. of Epsom salts in the extract. This is 0.24 per cent. of the Epsom salts present. If the extraction had been continued six hours longer, making a total of eight hours (the time used for extracting leather with alcohol), practically 1 per cent. of the Epsom salts present would have been extracted.

[1] H. R. Procter (Leather Industries Laboratory Book, p. 207-8) states that glucose is not absorbed by hide powder, but that on the other hand, it renders a portion of the hide powder soluble and thus increases the non-tannins. Other work has also been done which illustrates this fact; *Collegium*, 1903, pp. 114, 124; 1906, pp. 421, 432, 442, 443; 1907, pp. 50-56, 165.

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From these facts, it is evident that the method does not possess all of the advantages over the water extraction method which were claimed for it. For the sugars and Epsom salts are soluble to such a degree that there would be considerable error in the results given if these substances were assumed to be absent from the extract. And since Epsom salts, and especially glucose, have a decided but slow solubility in boiling 95 per cent. alcohol, it would seem probable that the end point of the extraction with 95 per cent. alcohol, of leathers containing Epsom salts and glucose would be less definite than the end point obtained by extracting the same leather with water.

THE COMPARATIVE EFFICIENCY OF CERTAIN TANNING MATERIALS.

By Robert W. Griffith.

The number of tanning materials which are offered to the tanner steadily increases and as the list extends so do the old time tannages of pure bark become less in evidence. Whether the gradual disappearance of the old tannages should be lamented as a sign of decadence in the art of tanning is questionable. The introduction of some new material is evidence of a certain progress and its successful use develops a keener intelligence. It is not conceded that in this industrial development the excellent qualities which distinguish leather from anything else have been sacrificed. On the contrary and as a result of this development the tanner has the choice of tanning materials which will equal the best bark tannage in producing any desirable quality in leather. But it would seem superfluous to enter into a defense of modern development at this stage.

Innumerable circumstances have conspired to bring about present conditions with the result that ocean freights have become an economical factor in the tanning industry and the tannery is no longer a portable proposition trailing the logging camp.

The experience accumulated in the process of development has not been without its price, and the characteristics peculiar to a new tanning material, the tanner has been obliged to ascer-

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tain for himself. Now that many of these new materials have a recognized value in the tanning industry, the question of their relative efficiency in the production of leather has to be considered. In judging the economy of various materials which, of course, includes the efficiency as well as the cost of the material, many points have to be remembered.

The analysis of the material offers a good indication of its tanning merits, but its efficiency in leather production has to be tested practically.

Some materials show a considerable difference between the amount of tannin as obtained by analysis and that available for producing leather. Myrobalans and Valonia are specimens of this type, and liquors prepared from these lose a great deal of their tanning strength on standing some time as is shown by the following experiment. A quantity of strong valonia liquor was freshly prepared in a cask and covered with a layer of oil about a quarter of an inch thick. No mould or decomposition showed itself during the experiment, and samples were taken for analyses from time to time.

The loss in tanning strength after standing 56 days amounted to 18.24 per cent. and after 91 days to 23 per cent. The insoluble matter precipitated in the liquor increased considerably. The following is the actual analysis:

ANALYSIS OF VALONIA LIQUOR.

	Fresh liquor	56 days after	91 days after
Tannin	14.64	11.97	11.40
Non-tannins	6.60	6.64	6.72
Insolubles	0.64	2.81	3.68
Water	78.12	78.58	78.20

An experiment was made with myrobalans under exactly similar conditions, but showed a loss in tannin strength, slightly less than valonia. After standing 53 days the loss in tannin strength amounted to 18.42 per cent., and after 90 days to 21.7 per cent. The following shows the actual analysis:

ANALYSIS OF MYROBALANS LIQUOR.

	Fresh liquor	After 53 days	After 90 days
Tannin	14.66	11.96	11.48
Non-tannins	5.98	7.58	7.48
Insolubles	1.52	2.81	3.06
Water	77.84	77.65	77.98

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In both the Valonia and Myrobalans liquors the precipitation of insoluble matter commenced after the first day and steadily increased. It is abundantly clear that in the case of liquors prepared from Valonia and Myrobalans that the insoluble matters are formed at the expense of the tannin and not entirely from the original non-tannin matters. It is demonstrated, also, that in practice it would not be economy to leach these materials in the usual way. The deposited matter must have some value in increasing the weight of leather, and the way in which this value is obtained is by the direct contact of the material ground up and used to "dust" in the layers and this results in the deposit of considerable "bloom" upon the surface of the leather.

Valonia and Myrobalans are perhaps exceptional materials in displaying the quality of precipitating insoluble matter, but all tannin liquors do the same, but to a considerably less extent. Certain of the tannin extracts like Quebracho Extract and Hemlock Extract deposit less insolubles on standing in liquors than any other material. Having considered the behavior of the tannin material in its own solution, the next point to investigate in order to arrive at its tanning efficiency, is its leather forming capability. The tannin contained in different materials show a different degree of attraction towards hide fiber, some displaying quick powers of penetration whilst others diffuse through the fiber very slowly. The colloidal character of the particular liquor is perhaps responsible for this, and the amount of non-tannin matter present in the liquor is to some extent an indication of its colloidal properties.

With a view to determine the behavior of certain tannin materials when in solution, towards hide substance, the writer, a few years ago in conjunction with Mr. John Youl, carried out a series of experiments on a practical scale.

In these experiments separate liquors of the different materials were prepared and the hides tanned throughout with the same material. Samples of the liquors were taken regularly and the liquors, having been prepared of the same tannin strength, determined by hide powder analysis, were all strengthened at intervals with the same amount of actual tannin.

As the tanning of the hides proceeded, samples were taken

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from the hides and the amount of tannin absorbed was determined by Kjeldahl's Method of Nitrogen Estimation. In this way the speed of tannin penetration could be observed as well as the extent to which the liquor exhausted its tannin strength. The following table shows the results obtained after 34 days:

Material	Bark. °	Tannin	Non-tannin	Insoluble	Per cent. tannin in hides
Valonia.....	12½	1.48	1.12	0.48	33.0
Myrobalans.....	12½	1.82	1.30	0.32	31.4
Oak bark.....	9	1.17	0.89	0.26	30.6
Quebracho ext..	4	1.01	0.35	0.06	38.4
Chestnut ext....	9	1.36	0.74	0.22	33.1
Oakwood ext....	12½	1.56	1.26	0.26	33.9
Hemlock ext....	9	1.15	1.21	0.14	32.9

The barkometer readings of the liquors are given to illustrate that they bear no relation whatever to the tannin strength.

It will be seen from the above table that the Quebracho liquor is the most exhausted of its tannin and the hide shows a corresponding larger absorption of tannin from this liquor or, in other words, the Quebracho tannin enters into combination with the hide to form leather quicker than any of the other six materials. Oak bark tannin is the slowest. There appears to be sound reason for the popularity of Quebracho Extract as a tanning material in this country, and for the purpose of illustrating the respective absorption of the tannin of the other materials by the hides, the following figures are given, obtained by calculation from the above table. For every 100 parts Quebracho Tannin absorbed by hide there are absorbed

86.0 parts valonia tannin
80.0 parts myrobalans tannin
79.6 parts oak bark tannin
86.0 parts chestnut tannin
88.0 parts oakwood tannin
85.0 parts hemlock tannin

The next table shows the condition of the liquors and the hides after 74 days. It should be explained that as the tanning was carried out in a single vat for each material it was necessary to reduce the volume of the liquor by taking from each vat an exact equal quantity of liquor, each time the liquor was strength-

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ened. It was, therefore, considered impractical to attempt to account for all the tannin used in the liquors.

Material	Tannin	Non-tannin	Insoluble	Per cent. tannin in hide
Valonia	2.27	1.77	1.04	40.6
Myrobalans	3.02	2.08	0.81	36.8
Oak bark	1.72	2.20	0.45	40.1
Quebracho ext	1.33	0.79	0.13	45.8
Chestnut ext	1.98	1.12	0.55	41.6
Oakwood ext	2.20	1.96	0.34	41.4
Hemlock ext	2.13	1.42	0.15	43.6

It will be observed that Quebracho tannin continues to keep ahead in its absorption by the hide, but at this stage Oak bark tannin has made some progress and myrobalans, which, after 34 days was close to Oak bark, is now the least of the absorbed tannins. The amount of tannin absorbed by the hide in the second period of 40 days is very little compared with the amount absorbed in the first period of 34 days. In fact, in every case considerably over 50 per cent. of the amount of tannin finally taken up by the hide is absorbed within the first 34 days. It is also demonstrated that by the use of certain materials which become readily absorbed by the hide the period of tanning is much shorter than with others, and it is unnecessary to give them all the same length of time. To renew the illustration of the comparative absorption, after 74 days, we have the following figures: For every 100 parts Quebracho Tannin absorbed there are absorbed:

88 parts valonia tannin
80 parts myrobalans tannin
87 parts oak bark tannin
90 parts chestnut tannin
90 parts oakwood tannin
95 parts hemlock tannin

Having regard to the fact that all the liquors were made up and strengthened with equal amounts of tannin, it would appear from the analyses of the liquors that the tannin of some materials is not available as readily as some others. For instance, Myrobalans tannin has been less exhausted than any other and produces more non-tannins and insolubles combined. Myrobalans, however, have some value as acid producers, surpassing all the

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others in this respect, but it is worth considering whether acid could not be obtained cheaper from another source.

In our experiments the hides were suspended on sticks for the first 34 days, and for the next 40 days were laid in the vat and handled frequently. Afterwards they passed through a series of four layer liquors and occupied in this process a further 44 days which completed the tannage. The following table shows the figures obtained from the actual weights of the hides.

	Wet weight of hides	Per cent. water	Calculated dry weight of hides	Wt. of rough leather produced	Per cent. water in rough leather
Valonia	23.660	72	6,568	16,299	18
Myrobalans.....	23.772	72	6,599	14,120	18
Oak bark.....	23.081	72	6,407	16,065	18
Quebracho ext..	23.419	72	6,501	15,791	18
Chestnut ext....	23.000	72	6,385	15,547	18
Oakwood ext...	24.001	72	6,662	16,304	18
Hemlock ext...	23.750	72	6,593	15,558	18

	Calculated dry weight of leather	Per cent. gain in leather formation	Calculated hide substance per cent.	Calculated tannin per cent.
Valonia	13.365	103.4	49.1	50.9
Myrobalans. ...	11.579	75.6	56.9	43.1
Oak bark	13.174	105.6	48.6	51.4
Quebracho ext..	12.949	99.1	50.2	49.8
Chestnut ext....	12.750	99.6	50.0	50.0
Oakwood ext....	13.370	100.7	49.9	50.1
Hemlock ext....	12.755	93.4	51.6	48.4

Except for moisture determinations there were no analyses made to arrive at the figures in the above table.

Samples were taken of the leather when the hides were removed from the last layer and those were analyzed in the usual way by Kjeldahling. The following table shows a comparison of the figures obtained by analysis and by direct weighing which show remarkably close results:

	By analyses		By weight	
Material	Hide substance	Tannin	Hide substance	Tannin
Valonia.....	50.6	49.4	49.1	50.9
Myrobalans	58.6	41.4	56.9	43.1
Oak bark	47.3	52.7	48.6	51.4
Quebracho ext..	47.5	52.5	50.2	49.8
Chestnut ext....	51.4	48.6	50.0	50.0
Oakwood ext....	50.3	49.7	49.9	50.1
Hemlock ext....	51.0	49.0	51.6	48.4

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To complete the illustration of the comparative absorption of the respective tannins from the basis of the Quebracho tannin, we obtain the following figures from the analysis of the final leather; For every 100 parts Quebracho tannin absorbed there are absorbed:

94 parts valonia
78.8 parts myrobalans
100.4 parts oak bark
92.5 parts chestnut
94.6 parts oakwood
93.2 parts hemlock

These figures indicate the actual combining value of the tannins as they are absorbed by hide fiber to form leather. In the final completion of the various tannages it seems that the tannin, or leather forming substances, of Oak Bark possesses the greatest affinity for hide fiber and has the greatest "combining value." Quebracho tannin runs remarkably close, however, and having regard to its quick powers of penetration, it probably constitutes the most valuable tannin in the economy of leather making. Myrobalans tannin has the least combining value of any of the materials employed.

It must be pointed out that the "combining value" of a tannin material does not, however, indicate its weighing properties. The quality in a tannin material which imparts weight is possessed by the non-tannin matters. Referring to the table showing the hide and leather weights, it will be seen in the column of Percentage Gain in leather formation that Oak Bark liquors possess the greatest weight giving value followed by Valonia and then Oakwood Extract. Myrobalans is the last in this respect also.

These percentage gains are calculated from the difference between the actual dry weight of the hides and the actual dry weight of leather obtained. The percentage hide substance in the leather is obtained by calculation of the dry weight of hide in the dry weight of leather, and the percentage of tannin is obtained by the difference between the dry weight of hide and the dry weight of leather calculated on the latter. Tannin implies leather forming substances.

It is reasonable to suppose that those materials which impart

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the greatest weight to leather by virtue of their non-tannins would also show the greatest loss by thoroughly washing the leather.

To test the accuracy of this view, a sample of each of the different leathers was ground up and well washed with cold distilled water. After having been dried, the samples on analysis showed the following loss by washing:

	Per cent.
Valonia	8.0
Myrobalans	2.6
Oak bark	8.0
Quebracho ext	3.2
Chestnut ext	5.4
Oakwood ext	8.1
Hemlock ext	5.8

The value of non-tannins in the direction of weight giving must always be considered so long as the yield of leather is calculated from weights, but it will be observed from the foregoing results that the behavior of these non-tannins towards hide substance are peculiar to the material from which they are derived, and non-tannins as such bear no relation whatever to each other, in which respect they resemble the tannin, so that a material like Myrobalans which is rich in these substances is not necessarily a weight giver.

The difficulty of determining the exact value of non-tannins is not simplified by reference to their solubility because a material like Valonia, which yields a large proportion of insoluble non-tannins, is also an excellent weight producer.

Because of the uncertain action of the non-tannins and the fact that the actual tannin itself contributes under certain conditions in some materials to increase the amount of non-tannins, it becomes impractical to account for each original tannin unit employed in producing leather and, furthermore, as the density of a tan liquor influences the solubility of its leather producing contents, the analysis of the material is at best only an indication of its tanning efficiency, but the behavior of a tanning material under laboratory conditions frequently suggests the manner of its application in practice to obtain the best results.

In the practice of tanning it is not customary to employ only

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one tanning material, although a one material tannage is quite practical, but the development of leather making is towards the use of a combination of extracts, and it is already demonstrated that by proper selection and manipulation of the highest efficiency in the art of tanning is being obtained.

THE PRINCIPLES OF LEATHER STUFFING.[1]

By Hugh Garner Bennett.

The stuffing of leather is an essential and critical operation in the various processes of currying, and it is the purpose of this article to point out the scientific principles which underlie this process in the varied forms in which it is found in the practical world. Stuffing leather consists in the permeation of the fibrous tissues with various kinds of greases. This addition of grease to leather has several objects in view, the relative importance of which depends upon the particular kind of leather which is being manufactured. The following, however, are the principal reasons:—

(a) To give to the leather a certain amount of pliability and flexibility. This is desired, in a greatly varying degree, in all curried leathers. The function of the grease from this standpoint is that of a lubricant. The fibers of the leather, and even the smaller fibrils which compose them, have been isolated one from another in the processes of liming and tanning, but, by stuffing, they become coated with the fats and thus glide easily over one another when bending the leather.

(*b*) To give water-proofness to the leather. A certain amount of water-proofness is required in all curried leathers, if only to enhance the wearing properties. In the case of upper leathers, of course, the quality of water-proofness is particularly to be desired so far as it is compatible with a pleasing finish and feel.

(*c*) To give a further tannage. It is not the intention of the writer to discuss in this article the theory of tanning, but there seems little doubt that in some cases the stuffing of leather with

[1] *The Leather Trades Review.*

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grease has an additional tanning effect, though, naturally, of a character differing from the primary tannage. Oil tannages are, of course, well known, their action being ascribed, at any rate partly, to the effect of aldehydes formed by the oxidation of the oil. In speaking of currying, Procter says:—"Even the possibility of an aldehyde tannage is not excluded, where the fiber is not already completely saturated with other tanning agents or where these agents, from their nature, have not so firm a hold on the fiber as to be incapable of being displaced by the action of aldehydes."

(*d*) To give weight to the leather. This object is placed last on the list, but it is certainly not least in practical importance. Most curried leathers are even yet bought and sold by weight, both in the rough and in the dressed condition, so that the addition of grease merely to give weight is a fairly obvious aim of the currier. There is, of course, a limit, according to the nature of the leather and the finish that is desired, so that the problem becomes one of making the leather take as much grease as possible without appearing greasy.

The stuffing of tanned leather is very much more easy than the penetration of pelts with oils and fats as in the case of the oil tannages. In the true oil tannages powerful mechanical treatment (stocks, drums, etc.) is absolutely necessary to bring about the penetration of the fats, but in tanned, or partly-tanned, leather the fibers are isolated, and, therefore, the impregnation with greases is much more easy to accomplish. There is, nevertheless, considerable difficulty in getting grease into leather. The penetration of oils and fats into dry leather is not so readily brought about as the penetration of water, and it is necessary for us to consider first of all why this is the case. Although both oil and water are liquids, the former has the greater "surface tension," and that is the reason for the greater difficulty in making it penetrate. The problem of stuffing leather, therefore, is the problem of dealing with the surface tension of the greases used, hence it is necessary that the nature of surface tension should be briefly explained, so that the different ways of overcoming it may be the more readily understood.

In the three states of matter—gaseous, liquid and solid—we

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now know that the particles may be considered to be in a state of motion. As the space between the particles is decreased, as in the compression of a gas, the forces of attraction between the particles are increased in magnitude, so much, indeed, as to cause deviation from the gas laws. The motion of the particles in virtue of their kinetic energy independently exercised creates a tendency to fill all available space. This is realized in the gaseous state, but in the liquid state the inter-molecular forces referred to above have attained such a magnitude that they more than counterbalance this tendency. The result of this large increase in the inter-molecular forces is that a liquid is subjected to a force—in many liquids of considerable magnitude—away from its surface towards the interior of a liquid. This force is known as the "internal pressure" of the liquid.

The existence of this pressure will be easily understood when we consider the difference between a particle in the center of the liquid and a particle at the surface. In the center the particle is surrounded on every hand by other particles, all of which attract in their particular direction. If these forces be resolved in any plane they will be found equal in opposite directions. The resultant is, therefore, that there is no force on the particle due to the attraction of other particles. Its motion is, consequently, due only to its own kinetic energy. In the case of a particle at the surface, however, there are particles surrounding it and attracting it only on one side. Those which pull parallel to the surface of the liquid naturally neutralize one another as before, but there is nothing to counteract the attraction of those which fall towards the center, and hence there is exercised on all particles at the surface a strong force inwards—the internal pressure of the liquid. It is in consequence of the resultant of this force—surface tension—that there is the tendency in liquids to decrease the amount of exposed surface, *i.e.*, to assume that condition or shape in which the surface area is at a minimum—the sphere. The effect known as "capillarity" is also a result of the tendency. We have in leather stuffing therefore to consider how to lower the surface tension of the oil in order to make easy the penetration of the grease. There are various methods by which the surface tension of liquids such as oil may be reduced, and each

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of these has been applied in practical currying. It is proposed now to consider these in turn.

I.—CONTACT WITH ANOTHER LIQUID.

For theoretical purposes it is often better to measure the surface tension of a liquid with reference to the vapor of that liquid, but in the case of oil, which possesses a small vapor pressure and a large surface tension, the practical problem is its surface tension with reference to air. This high surface tension of oil is effectively lowered for practical purposes by putting it in contact with another liquid—water.

With many pairs of liquids their surface tension one to another is practically zero—*e.g.*, alcohol and water. When shaken together they form an homogeneous mixture, and we say that they are "miscible in all proportions." With other pairs of liquids their surface tension one to another is not zero, but is very small. When such a pair is shaken together two layers separate again, but each layer contains a certain proportion of each liquid. A good illustration is a mixture of ether and water, which, after shaking together, gives a layer of water containing 10 per cent. of ether, and a layer of ether containing 3 per cent. of water. Such liquids are said to be "partially miscible," or "mutually soluble." With other pairs of liquids the surface tension between them is still very appreciable, though very much less than either to air. These are known as "non-miscible" liquids, but there is always some mutual solubility, which varies widely in degree, however, in different cases. Water and chloroform are ordinarily considered as non-miscible liquids, but an appreciable amount of each is dissolved in the other. Water and oil also fall into this last class. The surface tension between them is great, but it is very much less than between oil and air, so that for practical purposes the surface tension of oil is lowered by putting it in contact with water. In stuffing, therefore, the leather is used wet and the grease laid on and the goods hung up to dry. As the water dries out of the leather the grease takes its place following it easily into the leather and between the fibers. This contact with another liquid (water) is the method used for overcoming the surface tension of oil in the oiling of

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sole and dressing leather, and it is also the principle of "hand stuffing."

II.—RISE OF TEMPERATURE.

As the temperature of a liquid is raised, the kinetic energy of its particles is increased, the spaces between the particles is also increased, and, on the other hand, the molecular attractive forces are decreased. Rise of temperature in a liquid, therefore, makes it increasingly fluid and mobile, and causes it to approximate slowly to the gaseous state. This involves in consequence a lessening of the internal pressure of the liquid and of the surface tension. With oil we have these effects just as with other liquids. An increase of temperature makes the oil more fluid, so that it runs more freely, and accelerates penetration of the fibers. Hence this method of lowering the surface tension of grease by increasing its temperature has been applied practically in currying leather. It is the principle of what is known as the "burning in" process, which involves the employment of dry, warm leather and hot grease. The process is carried out usually in one of two ways. Either the leather is completely immersed for a short time in the hot grease, or the hot grease is poured on to the warm, dry leather, but in either case the grease penetrates the leather with comparative ease. A practical advantage of this principle is that it becomes possible to employ "hard greases," *i.e.*, those which are solid at ordinary temperatures.

III.—RISE IN TEMPERATURE WHEN IN CONTACT WITH ANOTHER LIQUID.

This method of lowering the surface tension of grease is a combination of the two previous methods. The influence of a temperature increase on the surface tension of two liquids depends entirely upon the nature of the liquids. Some liquids which are "miscible in all proportions" at ordinary temperatures, become "mutually soluble" at higher temperatures. It may happen, indeed, as in the curious case of nicotine and water, that at still higher temperatures the liquids are again miscible in all proportions. The terms "miscible," "partially miscible," etc., apply, therefore, only to a definite temperature. In the case of a

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great many pairs of liquids, however, the effect of a rise in temperature on the surface tension between them is similar to the effect of a temperature increase on their surface tension with reference to air, *i.e.*, heat very often lowers the surface tension between the liquids. With aniline and water, for example, there is a mutual solubility at ordinary temperatures, but at temperatures above 165° C. there is complete miscibility. With oil and water the effect is also in the same sense, though not to the same extent. Hence, although contact with water lowers the surface tension of oil, an increase of temperature lowers it still further, as well as making the grease more fluid. The combination of these two factors, therefore, of raised temperature and of contact with water, constitutes a very efficient method of overcoming the surface tension of grease, and of assisting in its penetration into leather. The combination of these two factors is involved in the practical method known as "drum-stuffing," in which both raised temperature and wet leather are employed.

IV.—INFLUENCE OF DISSOLVED SUBSTANCES.

It always happens that a solution has a different surface tension towards another liquid than the solvent alone. In many cases the effect of the dissolved substance is to lower the surface tension between the two liquids. A fourth method, therefore, of helping grease into leather would be to employ some substance, which on solution in water yields a lower surface tension with grease than does water alone. This is often carried out in practice, and is the principle which underlies the process of "fat-liquoring."

If two non-miscible liquids have their surface tension one to another lowered by the presence of some dissolved substance, and the mixture is then agitated very thoroughly, minute drops of one liquid are disseminated throughout the other liquid, and under appropriate conditions considerable time may elapse before these drops coalesce again to form an homogeneous layer, as is normal with non-miscible liquids. This mixture, indeed, may become so intimate that the product might almost be termed an homogeneous mass. Such mixtures are called "emulsions." In the case of oil and water, which is our practical problem, we can dissolve in the water various substances, such as soap, borax,

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soda, etc., which lower the surface tension between the water and oil, and give after thorough admixture emulsions of a more or less permanent character. If one employs a relatively large proportion of water, one obtains what is technically known as a "fat-liquor." Raised temperature is often conducive to emulsification, and the practical process of fat-liquoring usually involves, therefore, all of the three methods discussed above for lowering the surface tension of grease. The principle of fat-liquoring hence includes the use of raised temperature, contact with water, and substances dissolved in the water. Natural fat liquors, such as egg-yolk, milk, cream, etc., are often useful assistants in making artificial emulsions. The oxidized fatty acids, moreover, such as occur in dégras, seem very helpful in emulsifying grease.

There are, of course, other points which materially assist in ensuring good penetration of grease into leather. It is perhaps obvious to suggest that, where possible, oils with a naturally low surface tension should be chosen, or oils which readily emulsify. Mechanical motion is also a very valuable assistant in stuffing leather. In drum stuffing the motion to which the goods are subjected results in a more rapid assimilation of the oils and greases than can be the case with evaporation, as in hand stuffing. Drumming is often resorted to after "burning in," to complete the penetration of the grease, and the stuffed leather is frequently made wet before this drumming to assist in the same direction. Fat-liquoring is also usually accomplished in the drum. Naturally the leather itself is also a great factor. The amount of plumping in the limes and early tan-liquors, and the nature of the tannage, are the important factors in isolation of the hide fibers and consequent good penetration of grease.

PROGRESS OF THE CHEMISTRY OF TANNING IN 1908-9-10.[1]

By Franz Ch. Neuner.

I. WORK ON THE THEORY OF THE TANNING PROCESS AND RESEARCHES OF A GENERAL CHARACTER.

The difference of opinion as to tanning, whether it shall be

[1] Condensed from *Zeitschrift für Chemie und Industrie der Kolloide*, Feb. and March, 1911.

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considered a physical or a chemical process, continues, and appears likely long to continue. Like all contested scientific questions, this one occasions strenuous work in the opposing camps. E. Stiasny, who may be regarded as the chief advocate of the physical, colloid chemistry idea, still continues to elaborate[2] his theory, put forward as long ago as 1907.[3] According to this theory, tanning consists of two parts; first the adsorption of the dissolved colloid tanning materiais by the gelatine of the hide, and then an irreversible change of condition which the adsorbed tanning material suffers, without however becoming thereby chemically united to the hide. It is well known that however they may differ chemically, tanning solutions in general have a colloidal character.

The results of Stiasny's recent work[4] support his theory. Fahrion holds[5] that the hide fiber must be oxidized before or during the tanning process in order to make serviceable leather. This view is opposed by researches which show that the adsorption of acid, alkali and tan-stuffs by hide powder or hide is independent of any previous oxidation of the hide fiber. Stiasny shows further that the products of decomposition of collagen which undoubtedly contain the reactive groups NH_2 and COOH in freer form than the collagen itself, are not precipitated by tan-stuffs. The single exception to this is glutin, whose precipitates with tan-stuffs are now generally regarded as colloid precipitates. Acids are adsorbed much less freely by hide powder from alcoholic than from aqueous solutions, and in the former case no swelling takes place. Very recently Stiasny has shown that the adsorption curve holds for the taking up of acid by hide powder. R. A. Earp[6] has shown the application of the adsorption law for the equilibrium between water, tan-stuff and hide powder, while the non-tans show a much more crystalloid character.

In opposition to W. Fahrion[7] who holds that the surface development of the material to be tanned is of importance in the

[2] *Koll.-Zeit.* 2, Heft 9, (1908).
[3] *Chem. Ztg.*, No. 95 ff, (1907).
[4] *Coll.*, 1908, 117.
[5] *Zeit, f. angew. Chem.*, 665, (1903).
[6] *Coll.*, 1907, 175.
[7] *Zeit. f. angew Chem.*, 665, (1903).

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tanning process only in so far as it concerns the extent of the surface and the masses of the reacting parts, Stiasny shows that the *condition* of the surface is of great importance. H. Wislicenus[8] found that "sprouted" and ignited oxide of aluminum shows higher adsorption of tan-stuff than freshly precipitated hydroxide, although the latter certainly has the greater chemical activity. According to E. Stiasny[9] sprouted alumina takes more tan-stuff out of aqueous solutions than from solutions in glacial acetic acid, thus showing that the aqueous solution is colloid, while according to E. Paterno,[10] tannin in glacial acetic acid shows the molecular weight of digallic acid. He has also shown that hide takes less silicic acid from an α-silicic acid solution than from a β-silicic acid solution of the same concentration, the latter being colloid, while the former is not.

R. O. Hertzog in collaboration with J. Adler[11] and G. Rosenberg[12] has published two related contributions to our knowledge of the tanning process. He points out that the taking up of silver nitrate and certain dye-stuffs by hide powder are typical reversible adsorption processes. The taking up of phenol also apparently follows in the main the adsorption scheme, but the results obtained make it evident that other features are present. In the case of phenol the process is at least more complicated, and in the opinion of the author these irreversible processes can never depend solely on adsorption. The adsorption of colloids by hide powder follows the rule of W. B. Hardy, that oppositely charged colloids are adsorbed, while those similarly charged are not. In two cases (sugar and albumen solution) negative adsorption by hide powder may be observed. From this circumstance R. O. Hertzog[13] concluded that the surface of chromed hide powder must be covered with a more or less semi-permeable membrane which permits the passage of the solvent but not of the dissolved material.

Since further research shows that chromed and unchromed hide

[8] *Koll.-Zeit.*, 2, Sec. 1, (1907).
[9] *Coll.*, 1908, 117.
[10] *Zeit. f. phys. Chem.*, 4, 475, (1889).
[11] *Koll.-Zeit.*, 2, Sec. 2, III, (1908).
[12] *Koll.-Zeit.*, 7, 222, (1910).
[13] *Zeit. f. physiol Chem.*, 57, 315, (1908).

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powder are in essentially the same condition, Hertzog regards the question as no longer open. Stiasny[14] opposes this view of Hertzog. He also had found that white hide powder in the presence of albumen solution behaves entirely like chromed hide powder. The former indicates negative adsorption, although here one can scarcely suppose there is a semipermeable membrane. Hide powder takes from a solution of egg albumen as much water as white hide powder in a damp condition contains, that is, about 71 per cent., and this whether it is brought dry into contact with the solution or is moistened first.

E. Stiasny applies this apparent negative adsorption to the estimation of the plumping effect of acids.[15] It is clear that the hide powder must take away as much of the water of the acid albumen solution as its condition of plumpness due to the then present acid content permits. According to this research the water absorption depends on the increase of concentration of the albumen solution.

It appears from this that with increasing acid concentration from 0 to N/20 H_2SO_4, the plumping increases, reaching a maximum at about N/20 and decreasing again with further increase in acid concentration. The taking up of acid by hide powder follows fully the anticipated adsorption curve. An analogy in the behavior of hide powder with that of white hide cannot however be established. In the latter case, it is true, the water absorption by the white hide (plumping) also increases with increasing acid concentration, reaching a maximum at about N/10 H_2SO_4 (N/2 CH_3COOH). If the acid concentration is further increased, so great a decrease of plumping results that the hide may even shrink, that is, in consequence of the presence of a larger quantity of acid, the white hide holds less water than if it were in contact with water alone. The taking up of acid by white hide also follows the adsorption law, and for each acid there seems to be a maximum plumping concentration which is a specific constant of the acid.

An important contribution has been published by J. von Schroeder,[16] who has studied the adsorption of tannin under

[14] *Coll.*, 1909, 302.
[15] *Coll.*, 1909, 302.
[16] *Kolloidchem Beihefte*, 1, 1, (1909).

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various circumstances by charcoal, sprouted alumina, gelatine and hide powder, in order to draw inferences in regard to the nature of the tanning process. It was shown that the taking up of tannin from alcoholic solution by charcoal or sprouted alumina takes place in the manner of the adsorption process; that this also holds for water solution in the case of the sprouted alumina, while for charcoal and water solution it only holds in the case of extreme dilution. In the adsorption of tannin from water solution by sprouted alumina, the end concentration became constant after some time, (in the research in question, four days) but when charcoal was used as the adsorbent, the concentration of the tan solution continued to decrease during the whole time covered by the experiment.

Hide powder takes tannin from alcoholic solution according to the adsorption law only for the first hour; later the law does not apply. The same is true for water solution. The amount taken from alcoholic solution is much less than from water. The addition of acids scarcely influences the adsorption of tannins, while alkalies cause a marked decrease. The abundant formation of gallic acid in the process of adsorption of tannin from water solution by hide powder may be entirely suppressed by the addition of acid or by sterilizing the tannin solution and the hide powder.

The adsorption of tannin by gelatine follows the adsorption isotherm and appears independent of the previous history of the gelatine. (Fresh gelatine solution, gelatine jelly and soaped gelatine solution were used.) While inorganic acids do not hinder the precipitation of gelatine by tannin, organic acids have a great influence in this direction. In this case, however, the previous history of the gelatine has a notable effect; gelatine gel taking a higher acid concentration to hinder precipitation than soaped gelatine, which in turn requires more than freshly dissolved gelatine.

The glue-tannin precipitate, dried and extracted with alcohol, dissolves easily without residue in luke-warm water. This seems to prove that tannin can be completely washed out of the glue-tannin precipitate, that the components of this precipitate are loosely bound together, and that tannin is not adsorbed by gelatine from alcoholic solution.

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From these researches J. von Schroeder comes to the following conclusions. The adsorption of tannin by hide powder is a so-called indirect ("versteckte") colloid precipitation; that is, before the hide can be precipitated by tannin it must first be brought into a kind of soluble swelled condition. Therefore the taking up of tannin is far less when the hide powder is first treated with formaldehyde, because this makes the collagen completely insoluble. For a similar reason the taking up of tannin by hide powder proceeds much more slowly than in the case of glue. In the former case equilibrium is established much more slowly because in glue the collagen is already broken down, while in the case of the hide powder the outer layers must first become swollen before the precipitation of tannin by these layers takes place, and they in their turn because of their tanned condition hinder the swelling of the interior layers.

J. T. Wood[17] has also published an extensive research on the compounds of gelatine and tannin. Since various early writers gave very various figures for the proportions of gelatine and tannin in the gelatine-tannin precipitate, J. T. Wood reëxamined this matter, and found, as Sir Humphry Davy had, that the quantities of tannin precipitated depend on the concentration of the solution, and upon the amount of excess tannin. J. T. Wood's maximum to 100 parts gelatine was 240 parts tannin. According to Davy this should be 85 parts tannin, Lipowitz 65, Rideal 137, Mulder 135, Williams 78, and so on. By washing with cold and hot water until gelatine gives no precipitate in the wash water, a considerable part of the tannin is removed, so that the proportions in the washed precipitate were 100 parts gelatine to 136 parts tannin. The assertion of A. L. Lumiere and A. Seyewetz[18] that tannins and gallic acid render gelatine insoluble only in the presence of air was confirmed for gallic acid but negatived for tannin.

By chroming gelatine with solutions of chrome salts of varying concentration and basicity it was found that the Cr_2O_3 content of the resulting insoluble substance depends upon both the concentration and the basicity of the chrome solution, and

[17] *J. S. C. I.*, No. 30, (1908). (Reprinted in this JOURNAL, 1908, p. 183.)
[18] *Coll.*, 1906, 205.

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that this is true also for the chrome tannage of hide. It was shown also that the maximum given by Lumiere and Seyewetz[19] of 3.2 to 3.5 grams Cr_2O_3 per 100 grams of gelatine may be much exceeded, (up to 13.6 per cent. Cr_2O_3). Chromed gelatine takes as much tannin out of its solutions as unchromed. This is observable in the case of gelatine plates, which can take up less tannin than gelatine solutions. J. T. Wood inclined to the opinion that the basic chrome groups unite with the COOH group of the gelatine molecule, while the acid tannin molecule adhere to the amino group of the gelatine. The equal capacity for tannin of the chromed and unchromed gelatine would thus be explained. This view, which he had expressed tentatively, J. T. Wood abandons in a later paper[20] in which the gelatine-tannin precipitate is considered as a colloid precipitate. The necessity of the presence of an electrolyte[21] for the formation of the precipitate is explained as follows. According to Wo. Pauli,[22] perfectly salt free gelatine has no electric charge, but the positive charge conferred by the material adsorbed from the electrolyte first enables the gelatine to form a precipitate with the negative tannin. This precipitate then adsorbs more tannin, and hence appears a reason for the dependence of the quantity of combined tannin on the concentration of the tannin solution.

R. A. Earp[23] found that continued heating in water rendered gelatine insoluble, and that an old gelatine solution precipitates considerably less tannin than a fresh one.

Lüppo-Cramer[24] describes the tanning effect on gelatine of dissolved colloid Ag_2O and Ag_2O_2. The insoluble gelatine compound of silver superoxide is of surprising permanence. The oxides of mercury and copper also tan gelatine to complete insolubility. By treatment with alkalies, this tanned gelatine is detanned and brought into solution.

A. Ricevuto[25] investigated the influence of electric charge on

[19] *Bull. Soc. Chim.*, 1077, (1903).
[20] *Coll.*, 1908, 494.
[21] Weiske, *Zeit. f. physiol Chem.*, 7, 460.
[22] *Pflüger's Arch.*, 78, 315, (1899).
[23] *Coll.*, 1907, 379.
[24] *Coll.*, 1908, 24.
[25] *Koll.-Zeit.*, 3, 114, (1908).

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tanning. He found that gelatine solution only gives a precipitate with tannin when a *small* quantity of acid is added. With higher acid concentration, no precipitation takes place. This he explains by assuming that gelatine and tannin carry opposite electric charges only in the presence of low acid concentration. A substance must possess a negative electric charge in order to precipitate gelatine or hide. Therefore, Ricevuto asserts, chrome tannage must take place in alkaline solution in order for the chromic hydroxide to confer a negative charge.

Ricevuto's research, however, does not appear to justify the conclusion which he has drawn from it. This is especially true of the gelatine precipitate made with neutralized tannin solution.

Professor Henry R. Procter in "Problems of the Leather Industry," (Collegium, 1910, No. 313, reprinted in this JOURNAL, V. 242) makes some observations on the theory of the tanning process. In the case of tannage by sulphuric acid and salt pickle, he believes that the amphoteric hide forms a chemical compound with the acid, which is semipermeable to the salt and is dehydrated by its osmotic pressure. Aluminum and chrome salts, because of the weakness of their bases, are easily hydrolyzed. The hide takes up the free acid thus formed, as it does the acid from pickle, and fixes it. Continued hydrolysis results in the formation of colloid insoluble basic salts, which coat the hide fibers or possibly form adsorption or chemical compounds with them. Procter regards aldehyde tannage as essentially a chemical change, for "it is difficult to see how a volatile substance like formaldehyde can form a resistant coating on fibers."

B. Kohnstein[26] also gives a very interesting view of the probable nature of formaldehyde tannage. He considers that the condition of the fibers in formaldehyde leather is similar to that brought about by alcohol tannage, (according to F. Knapp), the gluing together of the fibers in drying being hindered by the union of the soluble protein of the hide with formaldehyde, forming a precipitate which surrounds the hide fibers,

On the contrary, L. Meunièr,[27] who has proposed a purely

[26] Personal communication.
[27] *Coll.*, 1908, 195.

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chemical theory for quinone tannage, thinks with U. J. Thuau that formaldehyde tannage consists purely of the adsorption by the hide fiber of colloidal polymerization products of formaldehyde.[28] Formaldehyde leather shows comparatively little resistance to warm water.

A new purely chemical theory of tannage has been proposed by L. Meunier and A. Seyewetz,[29] based on the observation that a leather can be made either with quinone in the presence of air, or with a weak alkaline solution of phenol, which has even greater resistance to boiling water than chrome leather. Meunier and Seyewetz have not only turned this discovery to practical account (see their patent described in this number of the JOURNAL), but also make use of it as the basis of a theory. They assume that the quinone oxidizes the animo group of the hide (the formation of hydrochinon was observed), and that this oxidized hide unites with a second quinone molecule.

The chief representative of the chemical conception of tanning is now, however, W. Fahrion, who supports his views with a very extensive and valuable array of facts. Especially valuable are Fahrion's researches on the nature of chamois tannage, which afford several new points of view. In 1903[30] he published his first comprehensive theory of tanning as a salt-formation between a tan-stuff and oxidized hide fiber. In 1908[31] he advocated the view that after the preliminary physical processes (diffusion, adsorption, etc.), the secondary phenomena are of a chemical nature. He held that these changes do not relate, as Stiasny thought, to the adsorbed tan-stuff alone, but also to the hide, in consequence of the chemical action of the tan-stuff. Fahrion especially urges the view that tanning is preceded by a partial hydrolysis of the proteid bodies in the hide, by which chemically active groups are formed which react with the tan-stuff. This conception is similar to Suida's[32] color theory, and as already mentioned is opposed by Stiasny.

[28] *Coll.*, 1909, 211 ff.
[29] *Coll.*, 1908, 195.
[30] *Zeit. f. angew. Chem.*, 665, (1903).
[31] *Chem. Ztg.*, No. 28, (1908).
[32] *Zeit. f. Farbenindustrie*, **2**, Heft 9, 257, (1908).

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Meanwhile W. Fahrion[33] published a new method of leather testing. In making tanning experiments with hide powder it is necessary to have some criterion by which to determine when the hide powder shall be said to be tanned. Fahrion uses for this purpose the behavior of the hide powder toward hot water. The hide powder is shaken up with water and then kept for 10 hours on a boiling water-bath, after which the percentage of dissolved organic matter is estimated, (called a). The undissolved part, expressed in per cent., $(100-a)$, is then the water resisting power, (Wasserbeständigkeit, "W. B."). The higher this number, the more complete is the true tannage in Fahrion's opinion. For pure white hide powder the W. B. is zero, and for quinone leather above 90. Between these lie the W. B. of vegetable tanned, oil tanned and chrome tanned leather, in an ascending series.

With the help of these criteria and many experiments, W. Fahrion comes to the following view in regard to the nature of the tanning process.[34] First it is granted that the primary process of tannage are of a physical nature. The preliminary processes depend on capillarity, diffusion and adsorption. The real tannage is a secondary process. Fahrion makes a distinction between true tannage, (which is a condensation process wherein the tan-stuff contributes O and the hide H to form water which splits off), and pseudo-tannage. The latter does not involve a chemical combination between hide and tan-stuff, but under the catalytic influence of the hide the tan-stuff splits off water, and the anhydro-derivative thus formed is precipitated in an insoluble condition on the hide. Fahrion's pseudo-tannage is comparable to Stiasny's secondary irreversible change of condition. Pseudo-tanned leather has slight water resistance, while that of really tanned leather is high.

1. *Chamois Tannage.*—True tannage is here brought about by the peroxyacids of marine animal oils, ("Tran"), which are formed by the oxidation of fatty acids in the air. The first phase of the reaction may be the union of the carboxyl group of the acid with a basic group of the hide. At least the deriva-

[33] *Coll.*, 1908, 495.

[34] *Zeit. f. angew. Chemie.*, 2083 ff., 2135, 2187 ff., 1909. *Coll.*, 1910, 16 ff., 249. Abstr. this JOURNAL, 1909, p. 326, 1910, pp. 72, 414.

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tives of the peroxyacids with replaced carboxyl hydrogen, (salts and esters), and also other colloid and unsaturated peroxides without the carboxyl group do not tan thoroughly, while leather tanned with the peroxyacids of marine animal oils shows high water resistance. All these peroxyacids which are used technically contain the group —O—O— at least twice. In the second stage of true tannage, an active oxygen atom of the peroxyacid oxidizes two NH_2 groups of two hide molecules to NH groups, and the resulting water in the form of OH + H saturates the two valences which have been freed by the splitting off of the active oxygen. This assumption of Fahrion's is supported by the observation that the percentage of active oxygen in the peroxyacid becomes notably less during the tannage, and is in analogy with the results of Bamberger's[85] researches on the oxidation of amino groups by active oxygen.

As a third phase in oil tannage, Fahrion supposes a complex body to be formed by the splitting off of a second O_2 group, which then combines with both of the NH groups. This conception is based provisionally on a supposed structural analogy with the dianilino-quinones, since the structure of the hide molecule is still so slightly investigated as to afford no sure basis for reasoning. Besides this true tannage there is a pseudo-tannage. W. Fahrion found in hide powder tanned with fatty acids of fish oils, a completely neutral nitrogen free oil, soluble in petroleum ether. Leather so tanned resembled chamois leather in appearance but had small water resistance. On further examination these oils proved to be rearranged fatty acids, lactones, some of which were insoluble in all solvents. As these lactones are formed first by means of the tanning process itself, the hide must have the power to split off water catalytically, and the insoluble lactone thus produced brings about the pseudo tannage of the precipitated hide.

2. *Aldehyde Tannage.*—Following Nierenstein's opinion, W. Fahrion conceives this to be a true tannage, for which the equation holds:—

$$HCHO + 2XNH_2 = H_2O + CH_2\,(NHX)_2.$$

3. *Quinone Tannage.*—Fahrion points out that during the pro-

[85] *Berl. Ber.*, 1898—1902.

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cess of quinone tannage, the proportion of active O in the quinone becomes less, and that by means of this O the quinone must operate to change the hide. The hide on its part must act through its amino group, since only such fibrous materials as contain the amino group (wool, silk, hide,) bring about the reduction of the quinone molecules. The analogy with di-anilino quinone is here closer than in the case of chamois tannage, and corresponds to the following equation for the true tannage:—

$$2XNH_2 + 2C_6H_4O_2 = C_6H_6O_2 + C_6H_4(ONHX)_2.$$

There is here also a pseudo tannage. Quinone when allowed to stand a long time with water forms an almost black amorphous body scarcely soluble in water which is freely taken up by hide powder, to which however it gives only a very slight water resistance.

4. Vegetable Tannage.—It is known that vegetable tan-stuffs are related to the phenols, while they contain no ready formed quinone. Since, however, tanning research with phenol shows that the water resistance of the product is in all cases proportional to the capacity of the reacting phenol to form quinones, Fahrion assumes that true vegetable tannage may likewise be conceived as quinone tannage, especially since he found that the *o-* and *p-* polyphenols are oxidized to quinones without atmospheric oxygen by water alone.

Beside this true tannage, which depends on the ability of the phenol derivative of tannin to form quinones, a pseudo tannage also takes place, through the agency of the phlobaphenes. "By the reaction between hide, tannin and water, a hydrolysis of the tannin takes place, and then under the catalytic influence of the hide, causing water to split off, the formation of a difficulty soluble anhydro derivative follows." By intensive action of water, this anhydro derivative is again hydrolyzed, and becomes easily soluble. Hence the possibility of detanning bark leather, and its comparatively low water resistance.

5. Mineral Tannage.—By researches similar to those for the other modes of tannage, W. Fahrion comes to the opinion that mineral tannage is first a pseudo tannage, and that it later passes over into true tannage. This is done by the hide splitting

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off water catalytically from the chrome salt in solution, and precipitating the anhydride so formed upon itself. This process is promoted by neutralization. Fahrion's views on mineral tannage are less convincing and his researches less extensive than on chamois tannage for example.

Among new tan-stuffs which have been investigated during the three years are the basic salts of the rare earths, cerium, lanthanum, etc., which in their tanning effect are very similar to chrome. F. Garelli[36] made some investigations, and shortly afterward his pupil, M. Parenzo[37] published the results of some tanning experiments with these materials. It was suggested that the abundant cerium bearing residues from monazite which has been worked for thoria (used in the manufacture of gas mantles) might be utilized as a source of tanning materials. It now seems probable that they will find a more profitable use in the manufacture of pyrophoric cerium alloys.

With the view that the adsorption of tanning materials depends chiefly on their physical properties, F. Neuner and E. Stiasny[38] studied the diffusive power of vegetable tan-stuffs, obtaining results as follows. Non-tans diffuse more rapidly than tannins, but a complete separation by dialysis is not practicable. The different tannins have considerably varying facility of diffusion through membranes, and many of them suffer in passing through a parchment membrane a partial splitting up into non-tans. In the case of many tannin solutions dialysis produces a cloudiness which seems to be due to diminished solubility caused by the removal of the more easily diffusible parts. In such cases the dialyzed solutions are sometimes difficult or impossible to detannize with hide powder. With increasing concentration and with increasing age of tannin solutions diffusive power decreases. By boiling solutions changed by age, the diffusive power may be restored. Sulphited quebracho shows less diffusive power than the untreated extract. From the diffusion of tan mixtures no conclusions can be drawn in regard to the conduct of the components. Non-tans seem to be without influence

[36] *Acad. dei Luicei,* vol. XVI, 1 sem. ser V.
[37] *Coll.,* 1910, 121.
[38] *Coll.,* 1910, 129.

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on the diffusive power of tannins. In the process of dialysis the parchment membrane increases in weight, the amount of increase varying considerably with different tannins.

In regard to the diffusion of chrome, iron and aluminum salts through gelatine jelly, H. R. Procter and D. J. Law[39] have made a report. They showed that the diffusion of acid and base proceed separately, as already suggested by E. Stiasny, because through hydrolysis the chrome salt is split into acid and base, and the former in conformity with its crystalline character diffuses much more rapidly in the jelly than the latter. The jelly was colored with weak phenolphthalein, so that the advance of the acid could be observed by the fading of the color and that of the chromic hydroxide by the green tint which it produced. In the case of chromium chloride solution, it was notable that the speed of diffusion both for acid and base appeared independent of the basicity of the solution, while for chrome alum solution only the acid diffusion was independent of the basicity, the speed of diffusion of the basic portion decreasing conspicuously with increasing basicity. A great difference was found between boiled and unboiled alum solutions. In the boiled solution the violet crystalloid modification being changed over into the green colloid form, the sulphuric acid now completely split off by hydrolysis showed a much increased rapidity of diffusion.

Of work of a general character there remains to be mentioned only that of L. Meunier and his pupils, which relates to the important subject of emulsions, treated from the standpoint of the tannery.

II.—GREEN HIDES AND THEIR PRESERVATION.[40]

The much disputed question of an interfibrillar substance in the hides of mammals appears now to have been solved by E. H B. van Lier.[41] It is a mucoid, similar to that found in sinews or the umbilical cord. It gives a weak acid reaction, is soluble in

[39] *J. S. C. I.*, Mar. 31, 1909. Reprint this JOURNAL, 1909, 157 and *Coll.*, 1909, 199.

[40] Pure theoretical researches on hide substance, having no direct relation to tanning, are not mentioned in this report.

[41] *Coll.*, 1908, 337.

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alkalies and in dilute lime-water and is precipitated by acetic acid. By long continued hydrolysis with dilute HCl it yields a substance which reduces Fehling's solution. The interfibrillar substance may be completely extracted from cow or horse hide by dilute lime-water in eight days. In this respect it is not identical with Reimer's[42] coriin which was apparently a decomposition product of connective tissue produced by the action of concentrated lime-water. The difference between sole and upper leather has often been explained as due to the presence or absence of this interfibrillar substance, determined by the previous treatment of the hide. Yet this explanation appears not to suffice, since the interfibrillar substance would doubtless be for the most part removed by liming. E. Stiasny and G. Abt,[43] in a work on the action of lime salt and acetic acid on green, sweated, limed or bated hide[44] come to a like conclusion about Reimer's coriin. The authors find that saturated lime solution exerts a solvent or hydrolytic action on hide fiber, and that this action continues during repeated extractions. The splitting up effect seems to be considerable. By fractional "salting out," primary and secondary gelatoses and gelatopeptones were recognized; also a compound of collagen and lime which may be called calcium albuminate. Lime-water shows a sterilizing action with reference to the ferments of the dung bate and of putrefaction. Salt solution, (10 per cent.), by itself has no solvent action on the hide substance. Repeated extractions with it gave less and less result in hide substance. Only when the hide without liming was put into the salt solution directly from the sweating or bating did the salt solution seem to dissolve any considerable amount of hide substance. This is really due to the insufficient sterilizing effect of the 10 per cent. salt solution. The hydrolysis of the so dissolved hide substance is slight, but is greater if there has been a previous liming. The degree of hydrolysis was estimated by Stiasny's method.[45] Acetic acid (N/10) produces a considerable swelling effect, but no great chemical change. The dis-

[42] *Coll.*, 1909, 321.
[43] *Dingl. polyt. Journ.*, 205, 143, (1872).
[44] *Coll.*, 1910, 189. Abstr. this JOURNAL, 1910, 384.
[45] *Coll.*, 1908, 371 and 1910, 181. Abstr. this JOURNAL, 1910, 345.

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solved portion is largely acido-gelatose. The action of bacteria in the sweated and bated hides is quickly checked.

The Brussels Congress of 1908[46] referred the question of proper preservation of hides to a commission, who should test the various methods of preservation and disinfection and work out new methods. This commission made a first report to the Paris Congress in 1910. J. Paessler reports on the damage to hides by unsuitable preservation.[47] S. R. Trotman[48] found that certain stains are due to microörganisms. J. Abt[49] finds two kinds of so-called salt stains. The first, gray and irregular, he ascribes to a yeast. The other, brown and visible on the flesh side, to various kinds of bacteria which act on the blood and make the coloring matter from it. A. Seymour-Jones[50] has studied the influence of mode of living and kind of food on the quality of sheepskins. He found that the cause of a frequently occurring eruption, ("Cockle"), was the feeding of the sheep on oil cake and other artificial foods. A few days after shearing the cockle disappears, and cockle is not found in goats or hairy sheep. Seymour-Jones suggests that the wool withdraws from the hide the more liquid parts of the fat, and that the excess of solid fat left behind is the cause of cockle. Breckle[51] suggests that the spores of authrax in hides may be destroyed by permitting the hides to lie in a warm damp room for some hours. The spores are thus made to germinate, and the resulting bacteria may be destroyed with lime.

J. H. Yocum[52] finds fault with the methods of disinfection suggested by the government, and recommends for wet salted hides immersion for five minutes in a 0.1 per cent. solution of bichloride of mercury saturated with common salt. The bichloride alone forms insoluble compounds with the hide. Not only

[46] *Coll.*, 1908, 398.

[47] *Ledertechnische Rundschau*, 1909, No. 51. Abstr. this JOUR., 1910, 198.

[48] *J. S. C. I.*, **28**, 1238. (1909). Reprint this JOURNAL, 1910, 216.

[49] *Le Cuir*, 1910, 527.

[50] *Coll.*, 1908, 191.

[51] *Zentralbl. f. Bact.*, **50**, 101, (1909)

[52] This JOURNAL, 1910, 507.

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does the salt prevent this, but the hides after immersion are as thoroughly salted as before.

III.—SOAKING, LIMING AND SWEATING.

L. Meunier and Hue[53] found that dry imported sheepskins which had been soaked, sweated, unwooled and again dried, lost when again soaked by the tanner from 25 to 30 per cent. They recommend the use of sulphurous or hydrochloric acid in the second soak. The skin substance which would otherwise be lost is thus converted into a gel, and in subsequent liming there is no more loss of skin substance than from fresh skins.

U. J. Thuau[54] describes the unhairing effect of sulphurous acid which acts chiefly on the Malpighian layer, and loosens the hair very well. For lessening or preventing swelling, common salt may be used. Further work on this line was done by E. Nihoul[55] who also used hydrochloric, acetic and formic acids, controlling the swelling by sodium sulphate etc. He attributes the effect to the ability of the acids to produce hydrolysis.

L. Levi and E. Manuel[56] find that high temperatures must be avoided in the use of technical arsenic sulphide and lime.

R. W. Griffith[57] gives a detailed explanation of the liming process from the scientific standpoint, with reference also to practice.

In order to estimate the quantity of dissolved hide substance in soaks and limes, R. A. Earp[58] precipitates the liquid with chrome alum and estimates the nitrogen in the precipitate by the Kjeldahl method. This method, however, does not precipitate the amino acids. F. Kopecky[59] titrates the soak water before and after use with normal acid, and finds in the difference between the amounts of acid used a measure of the dissolved hide substance, since the putrefaction of the hide forms alkaline substances.

[53] *Coll.*, 1909, 217. Abstr. this JOURNAL, 1909, 242.
[54] *Coll.*, 1908, 362. Abstr. this JOURNAL, 1908, 407.
[55] *Bourse aux Cuirs de Liege*, 1908, No. 38, 8.
[56] *Coll.*, 1910, 309.
[57] This JOURNAL, 1910, 109.
[58] *Coll.*, 1907, 412. Abstr. this JOUR., 1908, 63.
[59] *Coll.*, 1907, 311.

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J. T. Wood and S. R. Trotman[60] place 50 cc. of filtered lime liquor in a 100 cc. cylinder with 10 cc. glacial acetic acid and 40 cc. concentrated solution of common salt, and estimate the precipitate from its volume.

E. Stiasny[61] titrates the lime liquor with and without the addition of formaldehyde, and finds in the observed difference a measure of such material of an amino-acid character as has been produced by the hydrolysis of the hide. He supports his method by the results of a research by S. P. L. Sorensen.[62] This method however is not applicable to old limes which contain sodium sulphide. It is not practicable to remove this substance with zinc sulphate, for that would precipitate a part of the hide substance. E. Stiasny therefore recommends the destruction by means of iodine solution[63] of the H_2S released by acetic acid, neutralization of the acid, addition of formaldehyde and then titration with NaOH. This method is only available where amino acids are already formed. By completing the hydrolysis of an equal sample (boiling with 20 per cent. HCl) and subjecting it to the same analysis, the difference in the amounts of NaOH used gives a measure of the extent of the hydrolysis of the first sample. By determining the total N before and after complete hydrolysis, an estimate may be made of the proportions of mono-amino and di-amino acids in the decomposition products.

H. Garner Bennett[64] in the technical control of limes estimates their basicity by the use of methylorange and phenolphthalein as indicators. While phenolphthalein is only sensitive to the strong base, lime, methylorange also shows ammonia, amino-acids, peptone, etc. The difference between the amounts of acid used with the two indicators gives a measure of the dissolved hide substance. This very rapid method is not, as the author admits, very trustworthy. The end point is difficult to strike, and sodium sulphide exerts a disturbing effect.

H. G. Bennett[65] recommends a modification of the Kjeldahl

[60] *J. S. C. I.*, **28**, 1304, (1909). Reprint this JOURNAL, 1910, 272.
[61] *Coll.*, 1908, 371. Abstr. this JOUR., 1908, 398.
[62] *Biochem. Zeitschr.*, 1907, 45.
[63] *Coll.*, 1910, 181. Abstr. this JOUR., 1910, 345.
[64] *Coll.*, 1909, 194. Reprint this JOURNAL, 1909, 143.
[65] *Coll.*, 1909, 197. Reprint, this JOURNAL, 1909, 140.

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method. After the action of the sulphuric acid is complete, the mixture is neutralized with caustic soda, phenolphthalein as indicator, and then a neutral solution of formaldehyde is added, liberating the sulphuric acid of the ammonium sulphate, as shown:—

$2(NH_4)_2SO_4 + 6HCHO = 2H_2SO_4 + N(CH_2.N : CH_2)_3 + 6H_2O$. Hexamethylenetetramine is quite neutral to phenolphthalein, and free sulphuric acid is then titrated with soda.

IV.—DELIMING, PLUMPING AND PICKLING.

Of acids newly made available for these purposes, butyric acid has been prominently mentioned. It has lately been produced cheaply from distillery refuse by Effront's fermentation process, and is quite equal to other organic acids heretofore used, beside having valuable properties peculiar to itself.[65a]

E. Giusiana[66] uses sodium bisulphite for deliming, with an equal quantity of HCl. The sodium bisulphite forms with sodium sulphide and lime, H_2S, sodium sulphite, calcium sulphite and NaOH, which are changed into the respective chlorides by the HCl. This method avoids the danger of plumping by excess of HCl.

In the case of the acid swelling of white hide, R. W. Griffith and A. H. Claflin[67] found that the speed of plumping is directly proportional to the hydrion concentration. Gelatine and glucose do not diminish the plumping by acids, but they add to the restraining influence of NaCl. The influence of salts on acid plumping depends both on the nature of the salt and the kind of acid. In a 0.5 per cent. solution of sulphuric, formic, or lactic acid, 2.5 per cent. of sodium lactate prevents plumping, while 2.5 per cent. disodium phosphate hinders plumping in the case of formic and lactic acids, but not in the case of sulphuric acid. Analyses of sour yard liquors confirmed these observations. For example, a liquor containing 0.5 per cent. lactic acid and 0.5 per cent. calcium lactate showed no plumping effect.

[65a] Among the latter may be mentioned its odor, which is little short of terrifying. Ed.

[66] *Coll.*, 1910, 14. Abstr. this JOUR., 1910, 200.

[67] This JOURNAL, 1908, 154.

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A. Besson[68] has reported on the lactic acids and methods of analyzing them. The technical acid is digested with KOH. If this is done with boiling, the KOH acts on the foreign substances present, but if allowed to stand in the cold, the KOH takes up the lactic acids and hydrolizes the anhydrides without acting on the other substances.

V.—BACTERIOLOGY OF TANNING AND BATES.

Detailed researches on the role of bacteria in the tannery have been made by H. Becker,[69] G. Abt[70] and J. T. Wood.[71]

The action of microörganisms in destroying acid in tan-liquors was studied by L. Balderston,[72] who found that yeasts growing on the surface and not fermenting sugars, rapidly destroy the acid in liquors exposed to the air.

L. A. Groth[73] studied the influence of bacteria on tannin. Balland and Droz[74] recommended the use of a layer of oil on the surface of vats to prevent the growth of mold.

In recent years a number of artificial bates have been devised to replace the dung bates.

VI.—VEGETABLE TANNING MATERIALS.

Many researches on the constitution of the tannins, having no direct relation to practice, have been made. These are not mentioned.

J. Jedlicka[75] in an extensive research on the sugars of oakwood extract showed that the non-hydrolyzed non-tans of oakwood extract had a reducing power on Fehling's solution corresponding to an average content of 3.2 per cent. glucose in the extracts, while after hydrolysis the percentage of glucose rose to 7 per cent. This seems to mean that a part of the non-tans consists in the first instance of non-reducing di- and poly-saccharides.

[68] *Coll.*, 1910, 73.
[69] *Coll.*, 1909, 169.
[70] *LaHalle aux Cuirs*, 1909, 53, 87, 105. Abstr. this JOURNAL, 1909, pp. 86, 110, 165, 189.
[71] *J. S. C. I.*, 29, 666, No. 11, (1910). Reprint this JOURNAL, 1910, 366.
[72] This JOURNAL, 1910, 326.
[73] *Leather Trades Review*, 1910. Reprint this JOURNAL, 1910, 269.
[74] *Jour. Pharm et Chimie*, 1909, 6 Reihe, 29, 573.
[75] *Coll.*, 1909, 112. Abstr. this JOURNAL, 1909, 162.

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If the extract itself be hydrolyzed before being de-tannized, the percentage of glucose is 9.2 per cent. This higher proportion is explained by supposing either that a part of the saccharides are of a glucoside character, and are so combined with the tannin as to be precipitated by the hide powder; or that the removal of tannin with lead acetate also precipitates some gummy bodies which by subsequent treatment with sulphuric acid are converted into sugar.

(Here follows mention of many articles on the production of extracts etc., and of many patents relating to extracts.)

J. Paessler and Ch. Veit[76] have investigated the solubility of the commoner tanning extracts at various concentrations, and find that the "utilization," that is the proportion of really soluble tannin to that shown by analysis varies very much with different extracts. In some it is 100 per cent., but in most lower. In many it increases with increasing concentration of the solution, while with others it falls, and with still others it at first falls, and as the concentration is further increased it again rises.

In another study which deals with the colors which various tanning materials give to leather, J. Paessler[77] tested the leather colors in a Lovibond tintometer.

VII.—TANNIN ANALYSIS.

The official methods of the I. A. L. T. C. have now been published by authority of the Paris Congress, 1910. In 1908 Zeuthen[78] proposed an improvement in the official method, which was later modified by J. Paessler.[79] This method was tested by the commission of the I. A. L. T. C. on tannin analysis.[80] The A. L. C. A. has an official method of tannin analysis[81] which differs slightly from that of the I. A. L. T. C.

Karl J. Swick[82] proposes to make approximate determinations

[76] *Coll.*, 1908, 295. Abstr. this JOURNAL, 1908, p. 358.
[77] *Coll.*, 1908, 48. Abstr. this JOURNAL, 1908, 109.
[78] *Coll.*, 1908, 366. Abstr. this JOURNAL, 1908, 395.
[79] *Coll.*, 1909, 201, 305. Abstr. this JOURNAL, 1909, 298.
[80] *Coll.*, 1909, 201; 1910, 157. Abstr. this JOURNAL, 1909, 247, and 1910, 342.
[81] This JOURNAL, 1911, 3.
[82] *Coll.*, 1908, 281. Abstr. this JOURNAL, 1908, 355.

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of tannin content by examining the refractive index of solutions before and after treatment with hide powder, the fall in the index being approximately a measure of the tannin taken up. The instrument employed is the Zeiss immersion refractometer, with means for maintaining constant temperature.

R. Lepetit[83] precipitates tannin with ammoniacal zinc acetate solution. M. Philip[84] reports on certain color-relations of different tannins. E. Stiasny[85] found a very sensitive colloidal reaction with certain metallic salts. To 2-5 cc. of a dilute solution of an aluminum salt, 5 cc. of a 1/10 per cent. tannin solution is added followed by 10 cc N/1 Na_2SO_4, and the whole is boiled. A flocculent precipitate forms even when only 0.01 mgr. Al_2O_3 per cc. is present. This is regarded as a good test for the presence of genuine tannin.

H. Procter and S. Hirst[86] detected sulphite cellulose liquors in tanning extracts by means of the lignin reaction with anilin and HCl.

M. Nierenstein and T. A. Webster[87] give a chemical method of recognizing the adulteration of sumac depending on the fact that the pyrogallol tannin of sumac gives a precipitate with diazobenzol-chloride, while the catechol tannin of pistacia and other adulterants does not.

Cavazza[88] uses thallium carbonate and uranyl nitrate for the microchemical examination of various tanning materials. W. Appelius and F. Merkel[89] have prepared tables for the valuation of willow bark by von Schröder's hydrometer method. W. K Alsop[90] reports on the analysis of chestnut wood.

Much work has been done on color estimation of extracts. H. Procter[91] has devised a modification of the tintometer method, which English chemists have adopted.

[83] *Coll.*, 1910, 375. Abstr. this JOURNAL, 1910, 527.
[84] *Coll.*, 1909, 249. Abstr. this JOUR., 1909, 249.
[85] *Coll.*, 1908, 348. Abstr. this JOURNAL, 1908, 400.
[86] *J. S. C. I.*, 1909, 293. Reprint this JOURNAL, 1909, 146.
[87] *Coll.*, 1907, 244. Abstr. this JOURNAL, 1907, 308.
[88] *Chem. Zentralbl.*, 1, 1648, (1908). Abstr. this JOURNAL, 1908, 245.
[89] *Coll.*, 1909, 22. Abstr. this JOUR., 1909, 62.
[90] This JOUR., 1909, 95.
[91] *J. S. C. I.*, 1910, 663. Reprint this JOURNAL, 1910, 352, *Coll.*, 1910, 292.

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A. Gansser[92] employs "animalized" cotton fabric, while H. C. Reed and G. A. Kerr[93] use white woolen cloth for testing the coloring effect of extracts.

H. G. Bennett and C. D. Wilkinson[94] recommend the use of lead oxide for the estimation of acids in tan liquors, which precipitates the tannin and forms soluble salts with the organic acids. The quantity of these acids is estimated by titration with potassium ferro-cyanide.

A. Seymour-Jones and H. R. Procter[95] titrate the liquors direct with KOH, using fluorescin as indicator.

G. Grasser[96] proposes a method by which several of the acids often found in tan liquors may be estimated separately.

VIII.—VEGETABLE TANNAGE.

J. Gordon Parker[97] shows that sole leather tanned with liquors extracted at atmospheric pressure is firmer and has a higher water resistance than that tanned with materials extracted under pressure. The former kind he finds also tan more rapidly. He also decides that the value of non-tans in the tan-liquors, viewed from the standpoint of leather quality is at least extremely doubtful.

IX.—CHROME AND ALUM TANNAGE.

E. Stiasny[98] has published an extended study of the chemistry of chrome tanning. At the beginning of the one-bath process the sulphuric or hydrochloric acid from the hydrolized chrome salt is adsorbed because of its crystalloid character. Then adsorption of the basic chrome salt begins, an irreversible process, and this adsorption gradually increases. The basicity of the liquor therefore at first increases and afterward diminishes, and finally the liquors become more acid than at the beginning. The

[92] *Coll.*, 1909, 37.

[93] This JOURNAL, 1908, 382 and 1910, 94.

[94] *J. S. C. I.*, 1907, 1186. *Coll.*, 1907, 441. Abstr. this JOURNAL, 1908, 68.

[95] *Coll.*, 1910, 298. Abstr. this JOUR., 1910, 411.

[96] *Coll.*, 1910, 406. Abstr. this JOUR., 1910, 581.

[97] *J. S. C. I.*, 1910, 313. Reprint this JOURNAL, 1910, 297.

[98] *Der Gerber*, 1908, No. 823, 1909; Nos. 826, 827. Abstr. this JOURNAL, 1908, 401.

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more dilute the solution of chrome or aluminum alum, the more basic is the part taken up by hide powder. Added salts and colloids have no marked effect on the amount of chrome taken up. The addition of electrolytes to the first bath in the two-bath process causes a reduction in the amount of bichromate taken up, while the addition of mineral acids causes a great increase.

J. T. Wood and D. J. Law[99] report on a colorimetric method of determination of chrome in one-bath liquors, and H. Ballenbach[100] on a volumetric method with the use of potassium permanganate.

X.—LEATHER ANALYSES.

The Paris Congress of the I. A. L. T. C. appointed a commission to study the subject and work out an official method for the association. The official method of the A. L. C. A. was published.[101] For the qualitative estimation of grape sugar, in leather, B. Kohnstein[102] applies the Hoppe-Seyler method, employing orthonitrophenylpropiolic acid, which in alkaline solution reacts with grape sugar to form indigo. For the quantitative estimation of sugar, H. G. Bennett[103] recommends a modification. The copper oxide reduced in the Fehling's solution is shaken up with ferric sulphate, reducing an equivalent amount to ferrous sulphate, which is then titrated with potassium permanganate.

For the estimation of nitrogen in leather, U. J. Thuau and P. de Korsak[104] follow the usual Kjeldahl method as far as the formation of ammonium sulphate, which substance is broken up by sodium hypobromite and the released nitrogen measured in a specially constructed nitrometer.

XI.—MISCELLANEOUS.

Boulanger[105] has differentiated between the hide fiber and the cementing materials by means of the microscope, staining a thin

[99] *J. S. C. I.*, 1910, 398. Reprint this JOURNAL, 1910, 295.
[100] *Coll.*, 1907, 428. Abstr. this JOUR., 1908, 70.
[101] This JOURNAL, 1911, 12.
[102] *Coll.*, 1910, 310. Abstr. this JOUR., 1910, 467.
[103] *Coll.*, 1909, 289. Reprint this JOUR., 1909, 259.
[104] *Coll.*, 1910, 364. Abstr. this JOUR., 1910, 527.
[105] *Bull. Soc. Ind. du Nord de la France*, 1907.

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section of leather with Weigert's solution. He draws conclusions in regard to the swelling and tanning of the hide, and the constitution of corium.

M. C. Lamb[106] has made an extensive study of the injury done to book-binding leathers by the products of combustion of illuminating gas.

THE BACTERIOLOGY OF THE LEATHER INDUSTRY.[1]

(See J. S. C. I., June 15, 1910, pp. 666–672.)

By J. T. Wood.

BIBLIOGRAPHIC APPENDIX.

At the request of friends who are interested in the subject, I have been induced to print the following short bibliography of works bearing on the bacteriology of leather manufacture especially in connection with the bating or puering process. It was put together originally with a view to form part of a treatise on the subject, but as the prospect of publishing this is remote, I give the list as it stands in the hope that it may prove useful to other investigators. It does not profess to be complete, but I think it includes most of the important works. I shall be glad if those interested will inform me of any omissions, or make additions to the list, which will render it more complete.

For particulars of some of the earlier works (Nos. 1, 2, 4, 5, 6, 7, and 8) I am indebted to Dr. E. Stiasny of Leeds University.

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[1] From J. S. C. I. Supplement to article reprinted in this JOURNAL, 1910, p. 360.

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ABSTRACTS.

Depreciation of Skins in Process. CARL. E. SCHMIDT, in *Shoe and Leather Reporter,* March 6, 1911.—During storage and treatment, skins lose a part of their substance by liquefaction through the action of bacteria. This may be prevented by the use of zinc chloride, which is a deliquescent substance and must be bought in sealed bottles. The skins are first piled in low narrow piles after salting with coarse salt, and allowed to lie one or two days. The salt to be used for the second salting is sprinkled with a solution of 1 lb. zinc chloride in 1 gallon water until on squeezing the salt with the hands some liquid oozes out. Skins treated thus may be kept one year with practically no loss of skin substance.

If skins from a distance are found when received to have been heated so that the hair slips, they may be prevented from decaying further by dipping in a solution of 2 ounces of zinc chloride to a barrel of water.

A comparison of the zinc chloride method with the cold storage method was made. One lot of skins were kept at 30° F., another at zero F., and a third lot put in pack with zinc chloride as first described. At the end of a year the three lots were in equally good condition, and the leather made from the skins preserved with zinc chloride was in every respect equal to that made from fresh skins.

Fat-Liquoring. M. C. LAMB in the *Shoe and Leather Reporter,* March 16, 1911.—Incomplete absorption of the fat liquor by chrome leathers causes a greasy feel on the exterior and a "tinniness" or undertanned feel of the skin as a whole. This is sometimes due to insufficient neutralization, the acid acting upon the soap and oil emulsion and breaking it up, thus preventing penetration. Any over action of the borax or other neutralizing agent must be avoided, for if the leather is made alkaline the basicity of the contained chrome salt is changed and the leather will be rubbery if slightly alkaline, or it will seem undertanned if there is much excess of alkali. The writer approves of borax for neutralizing, but prefers sodium phosphate because it is less liable to produce the rubbery effect, and also because it is cheaper. If chrome leather is piled wet after neutralizing, dissociation of the contained chrome salts causes it to become acid again.

A soap and oil emulsion to be used as a fat liquor must not be in the slightest degree alkaline, or the dye will not hold on the leather. The writer prefers soft or potash soaps for making fat-liquors. Too much soap causes a cementing together of the fibers, producing a dead feel.

Acid fat-liquors possess some advantages over soap and oil emulsions. They work perfectly on leathers in which the acid is imperfectly neutralized. The material best known for this purpose is Turkey-red oil, prepared by sulphonating castor or olive oil. For the better class of leather, such as glace kid, sulphonated oils are not good enough lubri-

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cators, but this difficulty may be at least partly overcome by adding degras or neatsfoot.

A number of new materials unaffected by acids are now on the market, prepared by patented processes from mineral or resin oils by "saponification" under pressure. A properly fat-liquored skin should be completely penetrated, and every fiber lubricated.

New Qualitative Test for Tanning Materials. HUGH GARNER BENNETT in *Shoe and Leather Reporter,* March 16, 1911.—There are two types of tannins, called the pyrogallol and catechol tannins, the former yielding pyrogallol and the latter catechol on being heated to 200° C. Pyrogallol tannins deposit "bloom," (ellagic acid), give a blue black color with iron salts and no precipitate with bromine water and contain about 52 per cent. carbon. The catechol tannins yield no bloom, but deposit "reds," (phlobaphenes), give greenish black precipitates with iron salts and a precipitate with bromine water, and contain about 60 per cent of carbon. Some natural tanning materials seem to contain both classes of tannins, giving a blue black iron precipitate, and yet forming a precipitate with bromine water. Some writers class these as a third group.

The attempts at subdivisions of these main groups have not thus far been very successful. In the case of the catechol tannins, a division into two subgroups may be effected by the copper sulphate and ammonia test. A little copper sulphate is added to the tannin solution and then an excess of ammonia. The precipitate at first formed dissolves with excess of ammonia in the case of one group and does not in the other case. The color of the solution in the first case or of the undissolved precipitate in the other, helps in identifying the individual tannin. Other tests which are usually sufficient to complete the identification are made with vanillin, lime-water and sodium sulphate.

In the case of the pyrogallol tannins the copper ammonia precipitate is in every case insoluble in excess, and is in most cases very dark, so that there are few or no characteristic color reactions. All the important members of the pyrogallol group respond to the nitrous acid test, and none of them to the stannous chloride and hydrochloric acid test. The sulphuric acid test gives yellows or yellow browns in every case, so that none of these can be used in distinguishing the members of this group, neither do the color tests with sodium sulphite and with lime-water themselves serve as a basis of subdivision.

It is certain that with materials differing so widely as myrobalans and valonia, or sumac and chestnut extract, there must be some difference in chemical constitution. The subdivision of the pyrogallol tannins into at least two groups is made possible by the author's discovery of a new color reaction for solutions of tanning materials, which is carried out as follows. A solution of the tanning material is made of the same strength used for tannin determination. To a few cc. of this solution in a test-tube, an equal or somewhat smaller quantity of a 10 per cent. solution of sodium bisulphide is added, and after shaking one or two

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drops of a 10 per cent. solution of potassium chromate is added. With some tanning materials nothing is observed but a greenish or greenish brown color, evidently due to the reduction of the chromate to chromic salts by the sulphurous acid present. This is the behavior of all the catechol tannins examined by the writer. With some pyrogallol tannins a rich blood-red color is obtained, but this rapidly fades through orange to yellow brown. This transient blood-red color is characteristic of myrobalans, sumac and their extracts, of gallotannic acid and also of gallic acid. With other pyrogallol tannins a deep red violet color is obtained, which is much more permanent, and is easily destroyed by dilute mineral acids. This color is given by valonia and its extracts, by chestnut extract and by oakwood extract.

The Use of Sulphur Tannage in the Manufacture of Leather. W. EITNER. *Der Gerber,* **37,** 1-3, 15-17, 43-5, 59-61.—In reducing with sodium hyposulphite in the double bath chrome process, sulphur separates as a fine powder, a portion being included within the fiber of the leather. The author has earlier shown that this last involves a sort of tannage. Although sulphur is not a tanning agent, it acts like the flour used in glacé leather manufacture, making the leather soft and fuller. The product is analogous to the leather obtained by Knapp on treatment of hide with an alcoholic solution of stearic acid which is even useful for some manufacturers, for instance the valves of wind musical instruments. By using a solution of sulphur in CS_2 and evaporating, a leather may be obtained which can be staked and resembles stearine leather although not so soft.

The auxiliary tannage effected by sulphur is the cause of the double bath chrome leather being found suitable for check-straps; for driving belts such leather stretches too much. In France a special superior leather of this sort has been made for automobile pneumatic leather. In ordinary two bath chrome leather, the author found the ratio of Cr_2O_3: S to be 3.8: 0.2 per cent. or at the highest, 3.1: 0.8 while a French leather gave 3.0: 3.8 per cent. The best grade of French check straps analyzed 0.66 Cr_2O_3, 0.23 Al_2O_3, 2.82 per cent. S; the fat was slight, hence the sulphur must be the real softening agent.

To secure the maximum amount of sulphur *within* the leather and to avoid its deposit on the surface, it is desirable to reduce the amount of acid used in the second bath. One process reaches this result by partially tanning in the first bath which contains for 100 kg. pelt, 3 kg. chrome alum, 1 kg. bichromate; 2 kg. HCl; for the reducing bath, 150 l. water, 8 kg. hypo are used, without acid addition. No sulphur separates and the bath can be strengthened for re-use. The product contains only 0.7 per cent. S but this is all within the leather which is markedly soft. The green color of such leather is not liked in the trade, hence to secure a whiter product, the following process is substituted. Each kilo pelt is pickled with 1.5 l. water containing 20 per cent. NaCl, 5 per cent. H_2SO_4 for 1-2 hours, then 4 per cent. bichromate is gradually added. The re-

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ducing bath contains only hypo hence all the available acid for reduction is within the fiber, derived from the first bath. The leather ought to be well washed to remove SO_2 although manufacturers sometimes leave this to be neutralized in liquoring, thereby increasing rendement; the result is spew and spots on the leather which is hygroscopic.

Another method employed to increase the deposit of sulphur consists in treating the hide first with acid then with hypo, or in the reverse order, before the tannage proper. 100 k. pelt are drummed 3-4 hours with 100 l. H_2O, 20 k. NaCl, 8 k. HCl, or suspension vats are used. The drained pelts are next drummed 6 hours in 20 per cent. hypo and let stand 6 hours more. The reversed order of process is also employed. The same amount of hypo is gradually applied and then the acid bath which contains 3 parts salt to 1 of acid in order to raise the density of the liquor and prevent extraction of the hypo by diffusion. This second bath is always employed in vats, the drum agitation being unsuitable. By this process, the S content may be raised to 4 per cent. and the tannage rapidly finished with chrome or vegetable tan.

In the manufacture of automobile leather which is the most important application of sulphur tannage, a product is required which can withstand 60° C. for the "vulcanizing" or cementing of the rubber pneumatic. The sulphur of the leather itself facilitates this process; the leather must not contain free fat. For original material, steer or buffalo hides are best. The soaks are sharpened with sulphide and likewise the limes. Only the croupons are used and they are evenly shaved by hand or machine before the sulphur tannage. In this the hypo is applied first, 25 per cent., gradually. After the acid treatment, the hides go direct to a preliminary chrome bath, 1-2 days suspension. The tannage is best finished in a series of vats, but the drum may be used. A moderately basic Cr salt is needed since the leather is acid and a basic tannage at the finish determines the heat resistance of the leather. The salt is prepared by dissolving 10 parts chrome alum in 50 hot water, adding gradually 1 chalk; the solution is drawn off after settling of the gypsum. A soft white leather, but not so resistant to heat is obtained by a combined tannage of chrome and alumina salt. For the currying, a fat liquor is indispensable, but an excess of alkali is used; castor oil soap is used for its preparation.

The sulphur fore-tannage is also employed in the manufacture of check and hitching reins, etc., finishing with the double chrome bath, although this is an unnecessary complication since the special advantage of the second bath is already secured. These leathers which were formerly made exclusively by alum or alum-fat tannage are now most generally made by the sulphur fore-tannage, finishing with a combination of chrome and alumina; the alum gives the softness, the chrome the resistance and endurance. The currying is carried out in two stages to suit the varied requirements. For the soap liquor, 3 per cent. soap, 0.3 potash, 25 water (pelt = 100) are drummed until taken up. After partial drying, the desired fat is applied to the flesh and drummed in.

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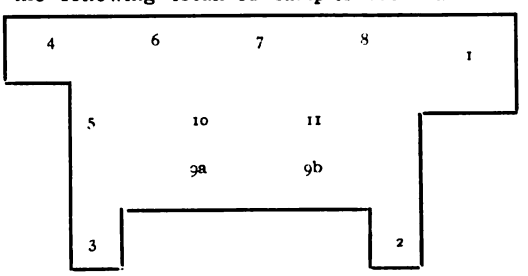
To make the leather look very dry and clear and yet give weight, a special grease is prepared by milling 10 parts stearine with 5 boiling water, then gradually adding 0.8 ammonia diluted with 3 parts water. This may be applied alone, after soap liquoring, after both soap liquor and greasing. The above dressings are all used above 37° C.

The combination of sulphur and vegetable tannage is of recent development. Steer or buffalo hides are used. Salted hides are given a lengthy liming; for foreign hides sulphide is added to the limes In England dung bates are used but not in France where a bate of 6 per cent. salt, 1.3 HCl (pelt = 100) is used. The sulphur tannage may be carried out in either order as described. Another variation consists in giving a light vegetable fore-tannage before the sulphur impregnation. The vegetable tannage proper is effected in vats or the drum, but the main difficulty is to avoid too rapid a saturation of tannin at the outset. A series of 10-14 vats are used, liquors 5-20°, barkometer. The tannage is finished in lay-aways or the drum. Formerly vegetable tanned rein leather was saturated with grease; even after the introduction of mineral tannage, sometimes as much as 25 per cent. was found. French leather now made by the combined process described gave 10 per cent. fats. If a soap stuffing be used, this must be neutral to avoid darkening the leather. W. J. K.

Leather Rendement and Examination. L. Jablonski. *Ledertechn. Rundschau,* 1911, 41-3.—Referring to the recent paper by Appelius and Manstetten (abstr. ante, p. 160), the author agrees that the practical yield cannot be deduced from the analytical rendement number. The analytical results have a value for the tanner, however, although not always appreciated. The rendement number is of no value whatever, but the tannage number is of fundamental importance not in giving actual weights, but ratios. The lack of agreement of the number determined by analysis with practical estimates is due to our imperfect knowledge of the composition of hide substance. The author believes it may be possible to ascertain the composition of the entire hide from the examination of an oriented sample and refers to the "Jahrbuch der Deutschen Leder industrie" for 1911 for details. His method (preliminary) is to determine hide substance, specific gravity and sometimes moisture in the following localized samples from a half hide:



(1) forehead, (2) forefoot, (3) hindfoot, (4) tail, (5) rump, (6)

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crup, (7) back, (8) shoulder, (9a) flank, (9b) belly, (10) (11) ribs, shell. A table of hide substance percentages in 3 ox hides is given; if these apparently irregular results are plotted graphically, complex curves but of very similar forms are obtained. Corresponding values from Appelius and Manstetten's data interpolate well. The usual assumption that an average of the analyses of various portions of the hide is representative, the author holds to be faulty; these variations here reach to 33 per cent. of the whole. The curve varies in type with different animals and some examples are given. Further investigation and reports are projected.

Fundamental Rules of Practice. (Continued.) L. MANSTETTEN. *Ledertechn. Rundschau*, 1910, 57-9.—Although a considerable amount of the substance dissolved at high temperatures separates on cooling, hot extraction is almost universal in practice. It has not yet been precisely ascertained at what stage the extraction ceases to be economical, hence the tendency is to push it in order to obtain everything useful, and on the other hand to let the extract settle well to obtain a clear solution.

The usual way of clearing is to allow the hot liquor from the spent bark to flow over less extracted bark and so on, in a battery or series of vats, thereby cooling, enriching and filtering the liquor. The filtering effect increases with the number of vats, but decreases with rapid flow. Since the usual practice is to hasten the extraction, slow filtration is not possible here and the liquor is unlikely to be well cleared when extraction and filtration are effected in the same round. Moreover the sediment deposited in filtration becomes redissolved in the hot extraction, leading to a great accumulation of difficult soluble matter.

The labor expended in carefully clearing a liquor is repaid by the rapid and perfect tannage. The so-called extract spots can be shown to be caused by separation of resinous, difficult soluble phlobaphenes, probably from poorly cleared liquors. The chief fault, however, is in employing hot liquors direct from the extraction. If warm liquors are to be used for steeping, these should have been previously completely cooled and filtered. To secure good clearing, the best plan is to conduct the extraction and filtration in two separate rounds, say 4 vats for hot extraction and 4 more for filtration of the product. Still better results are obtained by allowing a day's cooling and settling before filtration; the filter material is thereby kept cleaner for the hot extraction. The division between extraction and filtration not only gives better filtration but better extraction; the filter bark by transfer to the extraction vats becomes loosened. W. J. K.

Bacteria and Mould Fungi in Tanning. O. DROSIHN. *Ledertechn. Rundschau*, 1911, 59-60.—The author does not agree with Hugo Kühl that mould on leather originates from imperfect drying. He has repeatedly observed that leather stored through the winter and spring and apparently dry first showed mould during the sultry months of July and August. Not only the leather but the flooring, which was assuredly previously

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dry, was covered with mould. When vache leather moulds on storage during summer, the thinnest parts first mould, although they are naturally the driest. The germs of the growth may originate during the fermentation accompanying the tannage process and lie dormant, but the direct cause lies in the weather conditions and it is desirable that the subject be scientifically studied. It would be of interest to ascertain whether mould develops on leather which has been plumped with mineral acids. W. J. K.

The Pickling of Sheep Skins. *Lé March des cuirs,* **23,** (1911) 99-100.—After de-liming in a bran bate the skins may be preserved for some time in the soft condition by treatment with a pickle of 40 k. NaCl, 2.7 l. H_2SO_4, 400 l. H_2O. The salt is essential and must be maintained, else the pelt will swell. After thorough draining the pickled pelts are best stored in closed casks; moisture must be excluded. When required for tannage they are milled with 15 k. NaCl, 3 k. whiting, 400 l. H_2O and well rinsed. W. J. K.

Enzymatic Studies. S. P. L. SORENSEN. (Concluded.)—B. Colorimetric Method. a. Method employed. When a solution is to be examined, the ionic concentration of which is altogether unknown, preliminary trials are necessary to determine the liquids for comparison and the indicator suitable to the particular case. The most convenient method of operation is to commence by examining the reaction of the solution on litmus paper, if an alkaline reaction is obtained, several drops of phenolphthalein are added to the solution, if, however, the litmus shows an acid reaction, the behavior of the solution towards methylorange is determined. The result of these trials shows what other indicator to use in order to fix the ionic concentration more exactly. Suppose, for example, that we have found a reaction acid to litmus but alkaline to methyl-orange, and then with *p*-nitrophenol, the turning point of which is between that of litmus and that of methyl orange, the solution takes on a moderate yellow color. The ionic concentration of the solution is then such that *p*-nitrophenol will probably serve as the proper indicator for the measurement.

There are then measured out into test-tubes (of colorless glass and alike in all respects) the following mixtures of phosphates: pure primary phosphates, with 0.25 sec., 0.5 sec., 1 sec., 2-3-4 and 5 sec. (Note. The mixture 0.25 cc. of primary phosphate with 9.75 cc. of secondary phosphate is designated by the abbreviation "0.25 sec." and analogous abbreviations are used not only with phosphates, but also with those of glycocol, citrates and borates.) These mixtures correspond in ionic concentration to the region embraced by *p*-nitrophenol. A few drops of the indicator added to each of these mixtures gives a series of colors gradually increasing to deep yellow. After measuring similarly 10 cc. of the solution to be examined, there are added to each solution an equal number of drops of the indicator solution, and after

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mixing, the color of the solution which is being examined is compared with the series of standards.

If the solution examined is but faintly colored, more of the indicator may be added in equal amounts to all the tubes. If the color lies between that of two of the standard tubes, new standards may be mixed giving the interval more closely. The exponent of the hydrogen ions corresponding to the mixture whose color matches the solution examined can be found from the curves. (p. 136.) To make an accurate comparison, at least four standard solutions are necessary such that the color of the solution examined falls between the limits of the standards selected.

b. Sources of error of the method.

1. Color of the liquid itself.

If the solution examined is not colorless, it is necessary, before adding the indicator, to color the standard solutions as nearly as possible like the former, and then, to mask the inevitable slight differences of tint by using a large quantity of the indicator. For this purpose coloring matters may be used which may themselves be indicators, provided that their turning points are sufficiently removed from the ionic concentration of the solution. The following substances are available for this purpose.

(*a*) Bismark brown. (0.2 gr. in 1 liter aq.)
(*b*) Helianthin II. (0.2 gr. in 800 cc. alcohol, added to 200 cc. aq.)
(*c*) Tropeolin 0. (0.2 gr. in 1 liter aq.)
(*d*) Tropeolin 00. (0.2 gr. in 1 liter aq.)
(*e*) Curcumein. (0.2 gr. in 600 cc. alcohol, added to 400 cc. aq.)
(*f*) Methyl violet. (0.02 gr. in 1 liter aq.)
(*g*) Belgian blue. (0.1 gr. in 1 liter aq.)

In case the solution is turbid, an analogous turbidity must be produced in the standards. This has been done by means of freshly precipitated barium sulphate, prepared by mixing equal volumes of N/10 solutions of barium chloride and potassium sulphate. If more than a few drops of coloring solution or barium sulphate suspension must be added because of the strong color or turbidity in the solution being examined, then an equal number of drops of water must be added to it. Of course the accuracy of the method is greatly decreased by the necessity for such precautions.

2. Influence of neutral salts.

We have already seen, (pp. 134-135) the effect of neutral salts upon other methods for determining ionic concentration; in the colorimetric method also neutral salts may act in unequal ways, and, perhaps as well, differently upon different indicators. (Bohdan von Szyskowsky, Zeit. phys. Chem., 58, 420, (1907), and Lenor Michaelis and Peter Rona, Zeit. f. Elektrochem., 14, 251, (1908). This influence can be determined by a "blank test."

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3. Influence of toluene or chloroform.

Since toluene, chloroform or other antiseptics are often used in enzymatic studies, it is important to know whether the indicator employed is influenced by them. Experiments have shown that, in general, the acid indicators of the azo-group are not affected, while the basic members are quite useless. Further, phenolphthalein, *p*-nitrophenol rosolic acid, alizarin-sulphonic acid, and azo-lithmin are unaffected.

4. Modifications of the shade or of the intensity of the indicator.

If a few drops of methyl-violet are added to a N/10 solution of hydrochloric acid, the solution is colored green with a tinge of blue; but both the intensity and the shade gradually change. After an hour the solution is almost colorless. In using this indicator, therefore, as well as its analogs, mauvein, gentian violet, and methyl-green, which act the same way, it is necessary to work rapidly, and to be careful to add the indicator simultaneously to the solution and the standards. This bleaching is proportional to the ionic concentration, so that it is possible to work with precision even when the comparison is made after the lapse of considerable time. This modification of color, therefore, occasions less inconvenience than that from other causes.

It is otherwise, however, with indicators such as "Azosäureblau," chrysamine G, and pyrogallol-phthalein, with which the modifications of color depend on other factors than the hydrion concentration. Such indicators are useless for this purpose.

In case the indicator is difficultly soluble in water, a modification of color may result from the partial precipitation of the indicator. To use this class of indicators, they must be dissolved in rather dilute solution in alcohol, a procedure which involves an additional source of error, for it is scarcely probable that the hydrion concentration of the standards and the liquid investigated will be modified in the same way by the alcoholic solution.

Thus it is that on the one hand the acid indicators of the azo-group (tropeolin oo, for example) can generally be employed in the form of aqueous solutions, and give tints which are stable for a day at a time, while, on the other hand, the basic indicators of this same group (such as di-phenyl-amino-azo-benzene) must be used in alcoholic solutions, and give colors which gradually diminish in intensity due to the gradual precipitation of the indicator. The more complex the indicator, the less, generally, is its solubility in water, and the more, consequently, does this source of error make itself felt.

It may be added that, although phenolphthalein must be used in alcoholic solution, it is nevertheless sufficiently soluble in water so that the small additions necessary are not precipitated. On the contrary, in using the analogous and otherwise excellent indicator, thymolphthalein,[1]

[1] Made by Grüber & Co., Leipzig. Constitution not given. Its melting-point is 240°, so that it is doubtless different from the thymolphthalein prepared by P. Jakimowiez: *Ber.* **28**, 1876 (1895), which melts at 85°.

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this difficulty is encountered, so that one must work as rapidly as possible.

5. Influence of the proteins and their decomposition products.

A more important fact than any of the above, in colorimetric measurements, is that the proteins and their decomposition products often render the method difficult or even impossible. This is doubtless due, on the one hand, to the colloidal nature of the proteins and of a large number of the more complex indicators, and on the other hand, to the amphoteric character of the proteins whereby they can unite with both acid and basic coloring matters. Such combinations of protein and color-indicator are sometimes precipitated, but even if the combination remains dissolved—probably in the colloidal state—it generally presents a peculiar tint so that the colorimetric measurement becomes uncertain, or even valueless.

The behavior in this respect is very different with various groups of indicators. Methyl-violet, and its analogs are influenced only to a slight degree by the natural proteins, while the numerous indicators of the azo-group are almost all useless, in their presence. Here again the less complex indicators give the least error.

In taking account of the sources of error in the colorimetric method, it is seen what care is necessary in the choice of indicators, and how, if need arises, a comparison of electrometric and colorimetric methods must be employed in order to establish the value of the indicator chosen for the particular kind of solution with which one has to work. There arises then the question of what concordance must be obtained between the colorimetric and electrometric methods in order to establish the utility of a certain indicator. We have seen that in the measurement of protein solutions and the like, by the electrometric method, one can scarcely count on an accuracy greater than $\pm$ 0.05 in the exponent of the hydrogen ions. The colorimetric method is not as precise as this, both in principle and because its accuracy depends upon the electrometric method as the standard. We consider, therefore, that an indicator is suitable under the existing conditions when the variation between the measurements by the two methods does not exceed $\pm$ 0.1 in the hydrion index.

c. The indicators examined.

(The author here gives the results of his extended investigations on the applicability of a large number of indicators in the presence of various neutral salts and proteins, the hydrion index as determined by the indicator being compared with that determined by the electrometric method. As a result the following indicators are selected as giving results most free from the errors discussed above.)

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1.	Methyl-violet	$p_H^+ = 0.1—3.2$
2.	Mauvein	0.1—2.9
3.	Diphenylamino-azo-benzene	1.2—2.1
4.	Diphenylamino-azo-parabenzenesulphonic acid	1.4—2.6
5.	Diphenylamino-azo-metabenzenesulphonic acid	1.2—2.3
6.	Benzylanilino-azo-benzene	2.3—3.3
7.	Benzylanilino-azo-parabenzene sulphonic acid	1.9—3.3
8.	Metachlordiethylanilino-azo-parabenzenesulphonic acid	2.6—4.0
9.	Dimethylanilino-azo-benzene	2.9—4.0
10.	Dimethylanilino-azo-benzenesulphonic acid	3.1—4.4
11.	*a*-Naphthylamino-azo-benzene	3.7—5.0
12.	*a*-Naphthylamino-azo-parabenzenesulphonic acid	3.5—5.7
13.	*p*-Nitrophenol	5.0—7.0
14.	Neutral red	6.8—8.0
15.	Rosolic acid	6.9—8.0
16.	a-Naphthol-azo-parabenzenesulphonic acid	7.6—8.9
17.	Phenolphthalein	8.3—10.0
18.	Thymolpthalein	9.3—10.5
19.	*p*-Nitrobenzene-azo-salicyclic acid	10.1—12.1
20.	Resorcino-azo-parabenzene sulphonic acid	11.1—12.7

In the selection of an indicator from this list which we recommend it is necessary to make a judicious choice, taking especially the following facts into consideration:

a. The indicators of the methyl-violet group (Nos. 1 and 2) are particularly sensitive to the action of neutral salts; in addition it should be remarked that the color changes gradually, more rapidly the greater the acidity of the solution.

b. The basic indicators (Nos. 3, 6, 9, 11 and 14) dissolve in toluene or chloroform; in addition the first four separate partially from the solution on long standing.

c. In the presence of large amounts of natural proteins most of the indicators are useless, although several of them may serve; Nos. 1, 2, 13, 16, 17, 18.

d. In the presence of the products of protein decomposition, even in considerable proportion, the entire series of indicators may render real service; however, even in these conditions several of the acid azo-indicators can give rise to noticeable errors (Nos. 4, 5, 7, 8, 10) in which case one may have recourse to the corresponding basic indicators.

e. When the solution contains but small proportions of proteins or their decomposition products, the acid azo-indicators are usually preferable to the basic, because the former are not influenced by either toluene or chloroform, and because they do not separate from the solution on standing.

f. In all doubtful cases—for example in the colorimetric measurement of solutions whose behavior towards the indicator considered is un-

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known—the electrometric method should be used as a standard, and the value of the indicator determined by a comparison.

(Section C of the original paper deals with "The importance of hydrogen ion concentration in enzymatic reactions." Since the subject as treated hardly lies within the scope of this journal, the results will be given simply in the summary of the entire publication which follows.)

SUMMARY.

1. It is very necessary to distinguish between acidity and hydrogen-ion concentration; it is the latter alone which plays a role in enzymatic reactions.

2. When the normality of the hydrogen-ions is designated by 10^{-p}, we propose for the numerical value of the exponent the name "hydrion index," and the sign p_H^-.

3. In enzymatic reactions the mean hydrion concentration plays a role analogous to that of the temperature at which the experiment is performed. The hydrion concentration curve of an enzyme is that which is obtained by taking as ordinates the quantity of material split up in unit time under the conditions of the experiment, and as abscissae the mean hydrion index. The hydrion concentration curves proceed in a manner analogous to the temperature curves.

4. To measure the hydrion concentration of a solution any method whereby the ionic concentration changes during the operation cannot be used; consequently all the ordinary methods of acidimetry and alkalimetry are inapplicable. The "catalytic" methods also are not generally suitable; in rare cases they can be used only with all the requisite precautions.

5. As methods of measurement of the hydrion concentration in enzymatic reactions we recommend two procedures, each of which supplements the other: the electrometric method, very precise but rather complicated, and the colorimetric method, less precise but nevertheless extremely simple.

6. Electrometric method.

a. If π denotes the e.m.f. at 18° of a cell composed of a calomel electrode in N/10 potassium chloride and a hydrogen electrode (platinized platinum) in an electrolyte having a hydrion index p_H^+, we have seen that the equation

$$\pi = 0.3377 + 0.0577 \times p_H^+$$

expresses the relation at 18° between the e.m.f. of this element and the hydrion concentration of the electrolyte, if $p_H^+ - 0$, then $\pi_0 = 0.3377$.

b. In the principal table of curves (p. 136) the line which expresses graphically the above equation is designated by the name "line of exponents." With the aid of this line one can, in a manner purely graphic,

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without the need of any calculation, convert a measured value of π into the corresponding value of p_H^+ and conversely.

c. By electrometric measurements of the hydrion concentration of dilute caustic soda solutions the dissociation-constant of water was found to be $0.72 \times 10^{-14} = 10^{-14.14}$.

d. By dissolving in water certain substances of simple composition, substances whose purity can easily be verified and which can be obtained commercially of guaranteed purity, it is possible by mixing in determined proportions to prepare standard solutions having any hydrion concentration whatever between about 10^{-1} and 10^{-13}, exactly determined in advance by the electrometric method. On the principal table of curves one can easily read graphically the hydrion exponent of any one whatever of these mixtures.

The choice of the substances entering into these standard solutions has been confined to those that are protected against sudden changes in ionic concentration. We have shown the importance in enzymatic reactions of the presence of these "buffers."

e. We have cited a certain number of particular cases in which difficulties are encountered in the course of electrometric measurements of solutions such as are involved in enzymatic reactions.

7. Colorimetric method.

a. We have described the method to follow in colorimetric measurement where mixtures of the standard solutions mentioned serve as liquids for comparison.

b. The method is infected with a certain number of errors, the chief of which is due to the tendency of the natural proteins and their decomposition products to combine with the indicators, an inconvenience which in certain cases renders the colorimetric measurement difficult if not altogether impossible.

Because of these sources of error it has been necessary to verify with the greatest care just how far each indicator can serve under various conditions, with the view of rejecting those which are not useful, and of determining the degree of precision possible with those proving useful. In the control measurements the electrometric measurement of the hydrion concentration has served as the fundamental method.

c. The indicators examined, several of which have not been recognized hitherto, are divided, principally according to the position of the turning point, into five groups, for each of which we give a suitable choice of control measures effective at least for the most important and the best of the group.

d. Several of the common indicators, congo-red, for example, must be considered as altogether useless for measurements of this kind.

e. Based upon all the effective methods of control, we advise the use of twenty indicators. Since they are not equally available under all conditions it is necessary always, when it is a question of choosing an

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indicator appropriate to a given case, to take notice of a certain number of facts explicitly mentioned. See p. 263.

8. The importance of the concentration of the hydrogen-ions in decompositions by the aid of invertase, of catalase, and of pepsin, is shown by examples:

a. Under conditions otherwise equal, the optimum hydrion concentration for the inversion of sucrose has been recognized as very nearly independent of the kind and of the quantity of the invertase, as well as of the acid present. Under the conditions used the optimum ionic concentration of the inversion corresponds to $p_H^+ = 4.4$ to 4.6.

b. By a series of experiments upon invertase we have shown the necessity, in studies of reaction velocity, to take account of the hydrion concentration, and we have pointed out that the very different manners in which our predecessors have viewed the inversion of sucrose are attributable at least in part to the lack of recognition of the importance of the ionic concentration for this enzymatic reaction.

c. After having drawn attention to the importance of spontaneous decomposition of enzymes in studies of this nature, we have shown the resulting dependence between the length and the temperature of the experiment and the mean concentration of the hydrogen-ions.

According as the time is prolonged the optimum hydrion concentration is displaced towards the alkaline side.

d. At the temperature of 0° the optimum hydrion concentration of catalase is found near the neutral point, but a prolongation of the time appears to displace it towards the acid side.

e. At 37°, the optimum concentration for peptic decomposition is clearly dependent upon the time: for short duration the optimum point has a hydrion index slightly less than 2; but when it is prolonged, the optimum point is displaced towards the acid side.

J. H. H.

PATENTS.

Tanning. U. S. Patent No. 987,750. ALPHONSE SEYEWETZ and LOUIS MEUNIER, Lyons, France.

The method involves producing oxidation products of a phenol, including a substance of the quinone type, having a cyclic structure, and treating hide with the said products.

Process of Manufacturing New Organic Acids. U. S. Patent No. 988,032. HEINRICH ROSSNER and WILLIAM COTTON, Germany.

The process involves treating unsaturated fatty acids of high molecular weight, such as ricinoleic acid, in the presence of a mineral acid with formaldehyde or other body containing the carbonyl group, which renders them capable of combining with phenylhydrazine and hydroxylamine.

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Stretcher for Leather. U. S. Patent No. 988,331. E C. GREULICH and THEODORE G. STEINKE, Milwaukee, Wis.

Process of Tanning Leather. U. S. Patent No. 989,252. JABES A. HAMRICK, Hot Springs, Ark.

The hides are treated first with a liquor made from gambier extract, to which are afterward added at intervals extract of black alder, extract of persimmon and extract of black haw.

Machine for Treating Hides, Skins and Leather. U. S. Patent No. 989,278. DANIEL P. O'BRIEN, Woburn, Mass.

Combined Burette Holder and Pinch-cock. U. S. Patent No. 989,503. H. E. HILDEBRAND, Chicago, assignor to E. E. Behlke, Chicago.

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Journal of the

American Leather Chemists Association

Vol. VI JUNE, 1911 No. 6

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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ON THE ACTION OF DILUTE ACIDS AND SALT-SOLUTIONS UPON GELATINE.[1]

By Henry R. Procter.

The investigation which forms the subject of the following paper was begun in 1897, and much of the experimental work was done in 1898 in conjunction with Mr. Richard Paget, who, it was hoped, would share in the authorship of the paper. Circumstances, however, prevented its completion in coöperation, and the work has been carried on at intervals, with various assistance, up to the present time; and although there remain many points still unsolved, it seems desirable, in consideration of the present interest in colloid questions, no longer to delay the publication of what is already completed.

The investigation was originally undertaken in the hope that the study of comparatively simple cases of colloidal swelling and contraction might throw some light on the complicated phenomena of the tanning process, and especially on the very curious results of the treatment with acid and salt known as "pickling," and on the mineral tanning processes in which acids and salts are employed; but as it proceeded it became obvious that much wider and more important scientific issues were involved, which included the whole theory of colloid swelling.

The pickling process consists in principle in treatment of the skin with a very dilute bath of sulphuric acid, in which the connective tissue fibers are strongly swollen; and subsequent immersion in a concentrated solution of common salt, in which not merely the swelling disappears, but the fibers become greatly dehydrated, and the skin converted into a kind of leather. As even saturated solution of common salt has no dehydrating effect without the preliminary acid treatment, the effect is at first sight striking and unaccountable.

The swelling action is complicated in skin by its anatomical structure, which allows it to absorb liquids not merely by colloidal swelling, but capillarily in the interstices between the fibers, and it was obvious that no quantitative study could be made, unless

[1] This article was published in German in Kolloidchemische Beihefte, Bd. II, Heft 6-7, 1911. Professor Procter has kindly furnished the original manuscript for publication in the JOURNAL.

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means were devised to separate the two effects. Fortunately, however, gelatine behaves in a manner at least qualitatively identical with hide-fiber, and the very close chemical relationship between the two justifies the assumption that the same chemical affinities are involved, while from the absence of structure, capillar absorption is excluded. Comparative experiment confirmed this anticipated identity of behavior; and as the experiments were only intended as a preliminary investigation, ordinary commercial thin sheet gelatine was selected as a material. For the same reason, and to avoid complicating the work, slight variations of laboratory temperature, and other secondary disturbing causes such as adhering moisture, were neglected, and a method of experiment adopted which was capable of comparatively rapid execution. Sheets of thin French gelatine of the purest kind were cut, air-dry, to portions of about 1 gram in weight, and soaked in the requisite solutions, their gain in weight determined after draining as far as possible from adhering moisture, and both the gelatine and the residual solution analyzed as regards acid and salt, and the whole calculated to ash-free gelatine dried at 110°, and to milligram-molecules per gram. The air-dry gelatine in the earlier experiments contained 16.07 per cent. of moisture, which, as it was kept in a stoppered bottle was practically constant; and 1.19 per cent. of ash consisting mainly of lime with traces of sulphites and phosphates. It was, no doubt, a bone-gelatine. For all the earlier experimental work the same sample of gelatine was used, but for some later series of determinations other gelatines were employed of the same character but not actually of the same parcel. This may account for some variations between different series of experiments, while any single series gave as a rule very consistent curves.

The Swelling of Gelatine in Water.

The extent to which a gelatine will swell in cold water at a given temperature is to a great extent a specific quality of the particular sample, influenced by the proportion of partially hydrolyzed gelatine-products which are always present in the commercial article. These indeed cannot wholly be avoided, since they are formed to some extent whenever the gelatine jelly is heated so as to melt it, and they are unquestionably the main

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cause of those variations in character which have been attributed to what has been called the "*Vorgeschichte*" of the jelly. Traces of soluble electrolytes also affect it osmotically, and perhaps chemically. That gelatine and other gelatinizing substances do not swell to infinity, and become colloid solutions like gum and dextrine is due to the solid but elastic structure which is formed at setting, the cohesion of which finally balances the attraction of the gelatine for water. Under these circumstances it seemed not improbable that the swelling maximum of any given jelly would be influenced by the volume of its structure at the moment of setting; and this is proved to be the case by the following experiment.

Solutions containing approximately 5, 10 and 20 per cent. of air-dried gelatine were cast in glass tubes on wire spirals for convenience of handling, and were then dried for some days in a current of dry air, weighed, and allowed to soak in water at laboratory temperature, and weighed at intervals. Taking the weight of actual dry gelatine as unity the amounts of water absorbed were as follows:—

TABLE 1.—ABSORPTION OF WATER BY GELATINE.

	5 per cent.	10 per cent.	20 per cent.
Dried in air	0.1	0.1	0.2
After soaking 24 hours	8.4	4.3	3.7
After soaking 72 hours	11.7	6.0	5.1
After soaking 96 hours	12.6	6.5	5.4
After soaking 120 hours	13.2	6.9	5.5
After soaking 144 hours	13.6	7.2	5.7
After soaking 168 hours	14.6	7.7	5.8
In original jelly	23.2	11.1	5.0

As will be seen from the figures, and still more plainly from the graphic curves, the original setting volume has considerable influence on the maximum swelling, but is evidently not the sole determining cause.

Action of Alcohol on Gelatine Jelly.

It is well known that the swelling of gelatine jelly can be reduced by treatment with alcoholic solutions, and with absolute alcohol it becomes a hard and apparently dry mass. As there is no reason to suppose any chemical action of alcohol on gelatine, which on soaking in water returns to its original jelly-condition,

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the case seems a favorable one for the study of the effect of purely physical forces on jellies. Gelatine is practically quite insoluble in cold alcohol either pure or dilute, and conversely, even quite weak jellies are semipermeable to alcohol in solution. Alcohol placed in a porous cell lined with gelatine, and immersed in water, develops a considerable osmotic pressure, and masses of gelatine-jelly dehydrated by alcohol absorb scarcely any of the latter.

In order to get some idea of the effect of alcohol upon swelling, weighed portions of air-dried thin sheet gelatine were immersed in a series of mixtures of alcohol and water for 24 hours and again for 24 hours in renewed portions of the same solutions. This length of time had been found sufficient in previous experiments to establish practical equilibrium. The portions were then drained and weighed to determine the swelling; the gravity of residual alcohol taken, and its percentage calculated by the ordinary tables, and the pieces dissolved in hot water, and distilled to a volume of 25 cc. of distillate of which the gravity was taken to determine alcohol in the gelatine. Only in the case of the 100 per cent. alcohol did the gravity of the distillate fall so low as 0.999; and in this case only to 0.9979, so that any alcohol found may very well have been that merely adhering to the surface of the gelatine, and more exact methods of experiment must be adopted before conclusive evidence of any solubility of alcohol in gelatine-jelly can be obtained, though it seems possible that when the gelatine is nearly dehydrated, some alcohol is absorbed.

A second series of experiments were also made in a similar way, in which the gelatine was swollen in water for 24 hours before treatment with the alcoholic solutions. The results, which are given below are almost precisely similar to those of the first series, except that in the 90 per cent. and 100 per cent. alcohol complete equilibrium does not appear to have been reached. No evidence of penetration of the alcohol into the jelly was obtained, the gravities of the distillate ranging from 0.9996 to 1,000. The equilibrium appears to be completely reversible.

Table 2 and Fig. 1 give the weight of swollen gelatine obtained from 1 gram of dry. It will be observed that the curve is quite a regular one. The weight of the gelatine from

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absolute alcohol is slightly less than its weight air-dried.

TABLE 2.—ACTION OF MIXTURES OF ALCOHOL AND WATER.

Original mixture		Gelatine air-dry		Gelatine first swollen	
"absolute" alcohol cc.	water cc.	Per cent. alcohol in solution after soaking	Wt. of 1 grm. dry gelatine after soaking grms.	Per cent. alcohol in solution after soaking	Wt. of 1 grm. dry gelatine after soaking grms.
100	0	99.04	1.20	92.63	1.84
90	10	84.08	1.36	81.76	1.80
80	20	73.30	1.50	70.64	1.60
70	30	.....	....	60.88	1.68
60	40	51.56	1.70	48.73	1.96
50	50	43.04	2.24	39.80	2.36
40	60	33.22	2.86	30.84	2.52
30	70	24.46	3.14	22.77	3.06
20	80	16.20	3.72	15.17	4.42
10	90	7.93	5.72	7.42	5.96
0	100	0.00	7.23	0.00	7.23

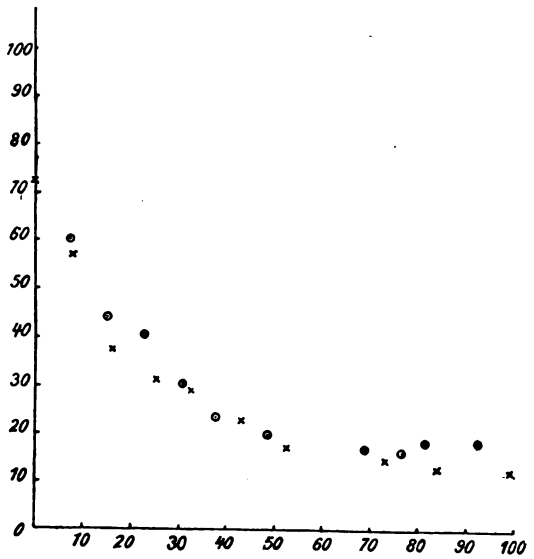

Fig. 1. (Table 2.)—Ordinates; weight of 10 g. dry gelatine after experiment o Abscissas; alcohol content of the solution after the experiment, in per cent. x = air-dry gelatine; • = previously swelled gelatine.

It is of course impossible to calculate theoretically the osmotic pressures of alcohol in such concentrated solutions as were here used, but the curve is such as would be expected from osmotic pressure acting on a material with a certain elastic rigidity of its

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own; and there seems no reason to invoke other forces. Probably if the osmotic pressures of the alcoholic solutions were independently determined, such experiments might furnish a means to calculate the elasticity of the jelly. Neglecting any small attraction of the alcohol for the gelatine, the equilibrium is probably

$$\left.\begin{matrix}\text{Cohesive attraction of jelly}\\ +\\ \text{Attraction of alcohol for water}\end{matrix}\right\} = \text{attraction of gelatine for water.}$$

This is of course merely an inverse way of stating the osmotic view, since osmotic pressures are "partial" kinetic pressures, and may be expressed as "minus internal pressures" of the solvent; just as in a mixture of air and water-vapor at atmospheric pressure, the pressure of air in the mixture is lowered by that of the water-vapor, which is equivalent to a minus atmospheric pressure.

Alcohol, though it precipitates hot gelatine solutions when added in large quantity, can be mixed in moderate proportions without causing separation, and the mass sets to an apparently homogeneous jelly, which, if alcohol is insoluble in jelly, must really consist of alcohol-water solution of such concentration as corresponds to the equilibrium just discussed, enclosed as an emulsion in a jelly-medium. Such an emulsion should swell more in water than a plain jelly, since not only will the jelly absorb all the water necessary for its maximum swelling, but the alcoholic emulsion-globules will become diluted, and exert an outward pressure on the jelly mass. On the other hand if the action of the alcohol were a chemical one, lessening the absorptive power of the gelatine, the swelling should be reduced whether the alcohol were introduced from without, or were already present in the mixture. Experimentally, it was found that of two somewhat concentrated jellies of equal strength, one made with water alone, and one with a mixture of water and alcohol, the latter swelled much the more, thus confirming the emulsion-character of alcoholic jellies. It is almost certain that such jellies would show microscopically the cellular structure which has been attributed by Bütschli and van Bemmelen to jellies in general.

The Action of Acids on Gelatine.

It is well known that gelatigenous fiber is swollen by all dilute

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acids which are sufficiently ionized, although very feeble acids such as boric, carbonic and sulphydric, have little or no swelling effect, and the same is true of many of the weaker organic acids.

Gelatine is similarly affected. A gelatine which absorbs 7 or 8 times its weight of pure water, may absorb over 50 times its weight of very dilute hydrochloric acid. For the most detailed experimental work, hydrochloric acid was chosen, as a highly ionized and typical monobasic acid, which could be easily estimated both acidimetrically and by silver nitrate. A further reason for the selection was that although in the commercial pickling process already mentioned sulphuric acid is used in conjunction with excess of common salt, yet the acid principally active must necessarily be hydrochloric; and as a satisfactory pickling can be produced by this and salt alone, nothing could be gained as regards principle by complicating the equilibrium with the presence of sulphuric acid and sulphates.

The general method of experiment was similar to that which has been already described. Pieces of air-dried sheet-gelatine of about 1 gram in weight, of which the content in dry ash-free gelatine was known, were soaked in solutions of acid of known volume and concentration for 48 hours, which was found a sufficient time to produce a steady equilibrium. The volume and strength of the residual solution was determined acidimetrically with standard KOH solution and phenolphthalein, the swelling of the jelly was measured by weighing after draining, and it was subsequently melted and the absorbed acid similarly titrated, it having been proved by preliminary experiments that the whole of the acid present could be thus determined, and that no difference in result was caused by melting the gelatine. Any slight variations from this procedure are noted in connection with special series of experiments.

In an early series of experiments it was found that though the whole of the acid present in the jelly was estimated using phenolphthalein as indicator, yet only a portion was determined when methyl-orange was used, although to free hydrochloric acid both indicators are equally sensitive. It is therefore clear that in the jelly a portion of acid is combined either chemically or by adsorption, in such a way that it is less ionized as regards H-ions than the remainder which behaves as if merely dissolved in the

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jelly, and of course varies with the degree of swelling. In order to get rid of the complication thus introduced, it was assumed as a first approximation that the absorbed volume of liquid was of the same concentration as that of the surrounding acid solution, and that the excess which was always found on the titration with phenolphthalein was "fixed" or more closely combined with the gelatine. This "fixed acid" proved to be usually somewhat lower but roughly approximate in quantity to that estimated by phenolphthalein but not by methyl-orange, and obviously represents the excess of acid absorbed by the gelatine, though it does not accurately determine what portion is attached to the gelatine and what to the absorbed water, and it will be shown later that the quantity of acid really fixed by the gelatine is greater than that so determined. Still it affords a ready means of comparing the character of the absorption; and as such, is given in the tables.

TABLE 3.—GELATINE AND HYDROCHLORIC ACID.

Series No.	Mgr-mols. HCl in 1 grm. solution after use Phenolphth. a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols HCl absorbed by 1 grm. dry gelatine Phenolphth. c	Mgr-mols. HCl absorbed by 1 grm. dry gelatine Methyl-or. d	Acid "fixed" by 1 grm. dry gelatine c—ab	Acid of 1 grm. dry gelatine not indicated by Methyl-or. c—d
XXVI 1	0.2692	18.25	5.780	.....	0.867	.....
XXVI 2	0.2089	17.72	4.460	.....	0.758	.....
XXVI 3	0.1546	18.23	3.613	.....	0.795	.....
XX 1	0.1425	21.70	3.798	.....	0.706	.....
XX 2	0.1250	21.35	3.400	.....	0.731	.....
X 1	0.1066	23.87	3.291	2.413	0.746	0.878
XXVI 4	0.1009	21.84	3.060	.....	0.856	.....
X 2	0.0879	25.27	2.989	2.074	0.768	0.915
X 3	0.0655	26.98	2.527	1.680	0.759	0.847
X 4	0.0548	29.56	2.392	1.568	0.772	0.824
XXVI 5	0.0483	31.33	2.387	.....	0.874	.....
X 5	0.0331	34.80	1.937	1.126	0.778	0.811
X 6	0.0134	45.31	1.431	0.609	0.824	0.822
X 7	0.0096	50.43	1.319	.....	0.835	.....
X 8	0.0060	54.16	1.176	.....	0.851	.....
XX 3	0.0028	45.38	0.963	.....	0.834	.....
X 9	0.0024	54.67	0.954	.....	0.823	.....
X 10	0.0006	35.27	0.622	.....	0.601	.....

Table 3 represents the results of more than one series of ex-

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periments, the Roman numerals of the first column indicating the series. These experiments were made in 1899 and 1900 on

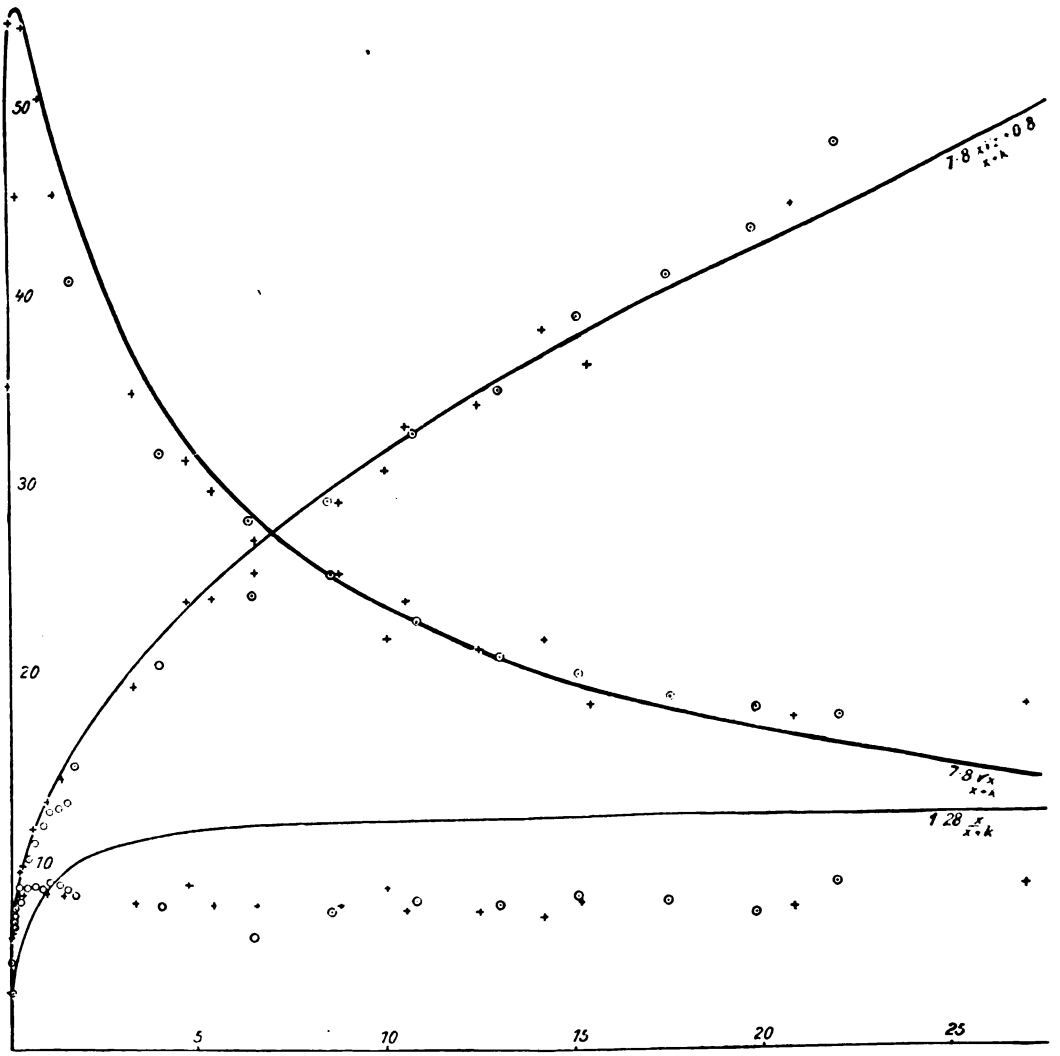

Fig. 2. (Table 3 and 4.)—Abscissas; mgr. molecules HCl in 1 gr. solution. Ordinates; + = results from table 3, • = results from table 4.

one sample of French gelatine, the titrations being done mostly by Mr. Pagett. Table 4 represents experiments made more re-

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TABLE 4.—GELATINE AND HYDROCHLORIC ACID.

Series No.		Mgr-mols. HCl in 1 grm. residual solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in 1 grm. solution (Methyl-orange.) d	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Methyl-orange.) e	Mgr-mols. difference HCl in gelatine (Phenolphth. and methyl-orange.) c—e	Mgr-mols. HCl in excess of solution absorbed by gelatine (Phenolphth.) c—ab	Mgr-mols. HCl in excess of sol. absorbed. Sol. estimated with m.-o. c—db
β	1	0.2217	17.63	4.790	0.2193	3.875	0.915	0.876	0.915
	2	0.1082	18.12	4.332	0.1064	3.203	1.129	0.734	0.773
	3	0.1755	18.74	4.089	0.1733	2.901	1.188	0.793	0.841
	4	0.1533	19.92	3.875	0.1516	2.706	1.169	0.817	0.855
	5	0.1306	20.74	3.485	0.1289	2.415	1.170	0.770	0.818
	6	0.1081	22.75	3.252	0.1066	2.064	1.188	0.788	0.827
	7	0.0801	25.13	2.901	0.0841	1.752	1.149	0.733	0.793
	8	0.0644	28.23	2.414	0.0625	1.480	0.934	0.593	0.650
	9	0.0403	31.65	2.045	0.0385	1.111	0.934	0.763	0.823
	10	0.0171	40.81	1.519	0.0154	0.565	0.944	0.821	0.890
α	1	0.0152	30.10	1.315	0.0142	0.610	0.705	0.857	0.888
	2	0.0129	32.28	1.298	0.0120	0.498	0.800	0.881	0.890
	3	0.0107	37.79	1.268	0.0098	0.520	0.748	0.899	0.903
	4	0.0084	38.37	1.196	0.0076	0.409	0.787	0.874	0.904
	5	0.0060	36.12	1.096	0.0054	0.352	0.744	0.877	0.901
	6	0.0041	37.94	1.016	0.0035	0.352	0.664	0.862	0.883
	7	0.0023	33.49	0.860	0.0018	0.194	0.666	0.783	0.793
	8	0.0015	31.15	0.751	0.0010	0.000	0.751	0.704	0.720
	9	0.0012	26.54	0.685	0.0007	0.000	0.685	0.655	0.668
	10	0.0006	18.36	0.467	0.0001	0.000	0.467	0.457	0.466
	11	0.0004	9.17	0.304	0.0000	0.000	0.304	0.300	0.304

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cently, with slight variations of method suggested by experience, on another sample of gelatine of a slightly more acid character, and with apparently a greater solid cohesion, as the maximal swelling is in all cases less, though the character of the curves and the position of the maxima in general show good agreement with the earlier results. Especially in the lower concentrations of Table 4 some ambiguity is caused by the acidity of the gelatine, consisting mainly of bisulphites which amounted to 0.282 mgr-mols. per gram as indicated by phenolphthalein, but did not affect methyl-orange, and of which at least a portion diffused into the outer solution, and affected its molecular acidity as determined by phenolphthalein, but could hardly have much influence on the acid "fixed." Determinations of the strength of the outer solution by methyl-orange, which certainly represent the whole of the acid present as HCl, are therefore given, with corresponding calculations of "fixed" acid, and of the acid absorbed in the gelatine as determined by the two indicators.

In reference to this work attention must be drawn to a paper[1] by Dr. Wolfgang Ostwald on the swelling of gelatine, in which he gives curves for the swelling of gelatine plates in acids and alkalies of different concentrations. In both cases he shows the existence of a maximum such as has just been described, but he also observed a minimum with very dilute solutions of which the present writer has found no trace. Ostwald himself ascribes this tentatively to the originally acid reaction of the gelatine, and in this he is probably correct, as the acidity is usually due to bisulphites, which are acid to strong bases and basic to strong acids, and of which neutralization in either sense would probably diminish the original swelling in water. The plates he employed were much thicker (3-4 mm. as compared to about 0.25 mm.) than those used in the present research, so that it is doubtful if real equilibrium was reached.

Table 5 gives the results of a series of experiments intended to test the reversibility of the equilibrium gelatine-acid-water. The gelatine was swollen for 48 hours in a solution which when equilibrium was reached was of 0.2253 mols. per mil concentration, and then for 24 hours in solutions of varied (lesser) con-

[1] Wo. Ostwald, Ueber den Einfluss von Säuren und Alkalien auf die Quellung der Gelatine. Archiv fur die ges. Physiologie. Bd 108. Bonn, 1905.

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centration. The latter time does not seem to have been quite sufficient for equilibrium to be again attained, but there is no reason to suppose the absorption as other than completely reversible. The lowness of the "fixed acid" as calculated by deducting the calculated acid of the solution absorbed is somewhat remarkable, and it is unfortunate that in this series no parallel determinations were made with methyl-orange. Several possible explanations may be suggested, but it seems best to defer discussion for further experimental investigation. The portions which were only treated for 48 hours in one solution are normal in respect of "fixed" acid.

TABLE 5.—GELATINE SOAKED FOR 48 HOURS IN HCl OF APPROX. 0.275 MGR-MOLS. PER GRAM, AND NOS. 4-16 AFTERWARDS FOR 24 HOURS IN WEAKER SOLUTION.

Series No.	Mgr-mols. HCl in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine. c−ab=f
1	0.2253	20.33	5.411	0.830
2	0.2253	20.14	5.411	0.873
3	0.2253	21.18	5.506	0.734
	Then 24 hours in weaker solutions.			
4	0.2333	22.00	5.683	0.541
5	0.2146	21.61	5.125	0.488
6	0.1950	21.10	4.616	0.502
7	0.1754	22.77	4.567	0.573
8	0.1561	23.44	4.274	0.615
9	0.1383	25.04	4.039	0.576
10	0.1182	24.37	3.531	0.650
11	0.0984	26.89	3.218	0.571
12	0.0807	27.90	2.944	0.692
13	0.0629	28.94	2.465	0.644
14	0.0526	29.33	2.220	0.673
15	0.0476	32.87	2.230	0.667
16	0.0462	31.18	2.083	0.643

Although no exact quantitative result can be expected from the somewhat crude method of experiment, it is evident that graphic plotting of Tables 3 and 4, Fig. 3, represents the curves of a regular equilibrium, the figures being fairly consistent for any one series of determinations, and the errors of experiment not greater

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than may be expected, considering the influence of various undetermined factors, such as the cohesive elasticity of the jelly, and the extremely small forces involved in considerable changes of volume near the swelling maximum. The approximately horizontal course of the "fixed acid" line, after a certain concentration of acid is reached, strongly suggests the idea of a definite though hydrolyzing chemical compound, rather than a merely physical one; and the determinations of "fixed acid" by the difference of reaction of phenolphthalein and methyl-orange prove a decided change of concentration of the H′ ion at or near that particular point. The occurrence of a very marked maximum of the swelling volume (S) is striking, and this follows naturally from the combination of the two regular curves, of "total acid" per gram of gelatine (a) and of "fixed acid" (f) since by the mode of calculation $S = \frac{a - f}{x}$; x being the concentration of the external solution given in column a.

As regards other acids, only a limited amount of work has been done. With weak acids like acetic and lactic, no definite maximum of swelling has been observed, the absorption of liquid increasing with the concentration till solution of the jelly begins. With formic acid a maximum occurs at a concentration of about 0.07 gram-mols. per liter, but it is less marked, and the rise to it is much more gradual than in the case of hydrochloric acid. Owing to the fact that no repression of swelling takes place with the weaker acids, a greater total swelling can be obtained by concentrating the solutions with acetic and probably with lactic acid than with hydrochloric, though it is evidently accompanied with greater solution, and possibly by structural changes of the gelatine.

As regards the fixation of acid, the methyl-orange method is inapplicable to any but the strongest acids, but calculating the absorbed solution as of equal strength to the external, figures for the excess-absorption are obtained which for acetic acid of medium concentrations are somewhat lower, and for lactic and formic about the same or slightly higher than those for hydrochloric. At the higher concentrations, the total absorbed acid is so large that experimental error makes the determination of "fixed acid" irregular and unreliable, and from the lowest concentrations the

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value rises to a fixed average much more gradually than in the case of strong acids.

As regards sulphuric acid, but few determinations have been made, but these show that it produces a maximum swelling effect at a low concentration of which the value has not yet been determined, and the apparently "fixed acid" is also somewhat larger. No experiments have yet been made on the determination of "fixed acid" by methyl-orange, but as the change of color of this indicator is gradual it is evident that determination by mere titration is somewhat rough, and it is proposed to investigate the subject further by the actual determination of ionization-constants.

The following tables 6-9 give the results of the work which has already been done on acids other than hydrochloric.

Table 10 (xxix 1-3) gives a few determinations on sheepskin and shows that a maximum exists, the weaker solution swelling more than the stronger; and the acid "fixed" is very similar in amount to that fixed by gelatine. The skin was unwoolled in the customary way, freed from lime, and dried at 80° C., and soaked in water till soft, before use.

TABLE 6.—GELATINE AND ACETIC ACID.

Series No.		Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid fixed by 1 grm. dry gelatine ca—b=f
XV	1	0.1050	46.97	5.570	0.638
	2	0.0873	44.29	4.520	0.653
	3	0.0693	43.90	3.747	0.705
	4	0.0513	37.27	2.527	0.615
	5	0.0340	32.98	1.679	0.558
	6	0.0161	25.36	0.874	0.466
		New Sample of Gelatine.			
A	1	1.0050	62.97	62.54	—0.74
	2	0.5083	57.28	32.05	+2.93
	3	0.2062	51.14	11.50	0.95
	4	0.1011	44.68	5.127	0.610
	5	0.0805	33.89	3.398	0.670
	6	0.0512	28.81	2.042	0.395
	7	0.0216	20.56	0.917	0.473
	8	0.0110	17.35	0.594	0.403

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TABLE 7.—Gelatine and Lactic Acid.

Series No.		Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab=f
XVII	1	0.1047	52.73	6.284	0.764
	2	0.0684	48.63	4.124	0.798
	3	0.0321	48.19	2.397	0.825
	4	0.0048	26.98	0.673	0.543

TABLE 8.— Gelatine (New Sample) and Formic Acid.

Series No.		Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab=f
B.	1	0.9918	47.90	48.01	0.48
	2	0.5196	49.74	26.16	0.31
	3	0.1910	53.95	11.33	0.97
	4	0.0786	55.92	5.236	0.838
	5	0.0511	55.47	3.669	0.834
	6	0.0196	47.31	1.640	0.711
	7	0.0146	41.40	1.064	0.464

TABLE 9.—Gelatine and Sulphuric Acid.

Series No.		½ mgr-mols. of acid in 1 grm. solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. of dry gelatine b	½ mgr-mols. of acid absorbed by 1 grm. of dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. of dry gelatine c—ab=f
XVI	1	0.1055	20.17	3.178	1.050
	2	0.0685	20.85	2.469	1.041
	3	0.0303	25.27	1.855	1.089
	4	0.0024	31.65	0.944	0.868

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TABLE 10.—SHEEP PELT DRIED AT 80° C. AND HYDROCHLORIC ACID.

Series No.		Original solution: Mgr-mols. HCl per grm.	Original solution: Mgr-mols. NaCl per grm.	Mgr-mols. HCl in solution a	Weight of solution absorbed by skin b	Mgr-mols. HCl absorbed by 1 grm. skin c	Acid "fixed" by 1 grm. skin c—ab=f
XXIX	1	0.1466	nil	0.1386	10.38	2.176	0.737
	2	0.0488	nil	0.0466	10.76	1.236	0.735
	3	0.0073	nil	0.0024	19.31	0.467	0.421
XXX	1	0.1807	3.00	0.1665	5.95	2.389	1.399
	2	0.0907	3.01	0.0798	5.70	1.499	1.044
	3	0.0378	3.02	0	4.71	0.364	0.364
XXXI	1	0.0692	4.17	0.0580	4.11	1.455	1.217
	2	0.0826	1.66	0.0700	4.27	1.315	1.016
	3	0.0981	0.48	0.0775	3.93	1.227	0.922

Attention must here be drawn to a research published by Stiasny on the absorption of water and acid by hide powder and ox-hide[4] by quite different methods to that adopted by the writer. From the data given it would be difficult or impossible to calculate the acid fixed, but the occurrence of a maximum of swelling in the weaker solutions is in both cases very clearly marked. The results with hide powder and ox-hide showed considerable divergence, which Stiasny attributes to difference in texture, but which perhaps may have been partly due to the time given having been insufficient to establish complete equilibrium.

One of the most striking effects of the "pickling process" which gave rise to the investigation is the extraordinary dehydration produced by the action of strong solutions of common salt on the acidified skin fiber, and also on the acidified gelatine; and acidified gelatine is also precipitated by it as a coherent mass from its warm solutions. No such effect is produced by common salt alone on neutral fiber or gelatine, the effect even of saturated solutions being somewhat to increase the swelling:—a gelatine absorbing about eight times its weight of water being capable of taking up about 11 of saturated common salt solution, and a larger quantity of one of medium dilution. The results of a

[1] Stiasny. Ueber negative Adsorption, und die Bestimmung der Schwellwirkung von Säuren auf Hautpulver und Blosse. *Gerber*, 1909, p. 183 et seq., and *Collegium*, 1909, p. 302 et seq.

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series of experiments are given in Table 11. Some other salts, however, and notably ammonium sulphate and some other sulphates, are well known to exercise a powerful dehydrating effect on swollen gelatine or skin, and even to precipitate gelatine from strong warm solutions as a coherent mass. The discussion of these actions of neutral salts must be deferred till the effects of salts in acidified solutions has been more fully considered. It may be pointed out, however, that the effect is most noticeable in the case of sulphates of weak bases, such as ammonium and zinc.

It is unimportant whether the gelatine or skin-fiber is first swollen by acid and then submitted to the action of salt-solution, or the proceeding is reversed, since similar effects are produced by the addition of a suitable quantity of acid to the already salted gelatine, and an effective pickling may be produced by adding a calculated quantity of acid to skins placed in a strong brine, although commercially the method is more costly. The quantity of acid which is most effective is larger than that required to produce a maximum swelling, since the presence of salt enables the skin or gelatine to "fix" a larger quantity of acid than it can do in an equally dilute acid solution without salt. In presence of sufficient salt, however, the necessary quantity of acid may be, (and commercially usually is) largely exceeded without much interfering with the result, though large excess is undesirable, and, in dilute salt solutions diminishes the dehydration. Some instances of the action of acidified salt-solutions on skin are given in Table 10 (XXX and XXXI); and the results of much experimental work on gelatine in presence of hydrochloric acid and salt in different proportions in Tables 12 and 13.

TABLE XI.—GELATINE AND VARYING SALT SOLUTION.

	Series No.	Mgr mols. NaCl in solution	Weight of solution absorbed by 1 grm. dry gelatine	Mgr-mols NaCl in swollen jelly of 1 grm. dry gelatine	Salt in excess of that calculated in absorbed solution
I	1	3.633	11.90	47.21	3.98
	2	3.035	14.72	48.41	3.73
	3	2.383	17.08	41.22	0.52
	4	1.665	16.42	27.80	0.46
	5	0.876	15.11	13.66	0.42
	6	0	8.83	0	0

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TABLE 12.—GELATINE, HCl AND NaCl. ACID APPROXIMATELY CONSTANT, SALT VARIED. THE ORIGINAL ACID WAS IN ALL CASES OF A CONCENTRATION OF 0.0921 MGR-MOLS. PER GRM. ON THE WATER EMPLOYED, AND THE VARIATIONS ARE CAUSED BY THE ADDITION OF SALT, AND THE FIXATION OF ACID BY THE GELATINE DURING THE EXPERIMENT.

Series	No.	Mgr-mols. original HCl per grm. solution	Mgr-mols original NaCl per grm. solution	Mgr-mols. HCl in 1 grm. sol. after use (Phenolphth.) a	Weight of sol. absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in jelly of 1 grm. dry (methyl-or.) d	Diff. mols. HCl by methyl-or. and (phenolphth.) c—d	Diff. mols. HCl found and calculated from solution absorbed c—ab	Diff. mols. NaCl found and calculated from solution absorbed e
V	1	0.0694	4.172	0.0628	1.251	1.331	.....	.....	1.252	—0.488
	2	0.0723	3.624	0.0677	2.487	1.377	.....	.....	1.209	—0.362
	3	0.0757	3.027	0.0696	3.197	1.336	.....	.....	1.114	—0.561
	4	0.0790	2.376	0.0758	3.667	1.331	.....	.....	1.053	—0.298
	5	0.0829	1.661	0.0793	2.976	1.270	.....	.....	1.034	—1.127
	6	0.0871	0.873	0.0834	13.096	1.935	.....	.....	0.926	—1.104
VI	1	0.0667	4.676	0.0633	1.144	1.313	0.408	0.905	1.241	—1.258
	2	0.0694	4.172	0.0631	1.126	1.317	0.750	0.567	1.246	—0.607
	3	0.0723	3.624	0.0657	1.275	1.280	0.623	0.657	1.196	—0.325
	4	0.0755	3.027	0.0688	1.343	1.249	0.478	0.771	1.157	—0.472
	5	0.0790	2.376	0.0741	1.962	1.255	0.710	0.545	1.110	—0.344
	6	0.0829	1.661	0.0761	2.816	1.278	0.507	0.771	1.064	—0.670
	7	0.0871	0.873	0.0814	10.330	1.831	1.020	0.631	0.990	—0.218
	8	0.0894	0.445	0.0853	19.90	2.638	1.640	0.998	0.941	—0.314
	9	0.0921	.....	0.0893	31.56	3.525	2.807	0.718	0.707	.....

NOTE:—It would be desirable to repeat the determinations of this table with precautions to ensure that the acid was really constant *after equilibrium was established.* Comparison with Table 13 shows, however, that the comparatively small variations of acid have in this case but little influence on the results obtained.

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TABLE 13.—GELATINE, HCl AND NaCl. ACID VARIED, SALT APPROXIMATELY CONSTANT. THE AMOUNT OF ACID IS DETERMINED AFTER EQUILIBRIUM IS ESTABLISHED, THAT OF SALT IS CALCULATED ON THE ORIGINAL SOLUTION, AS FIXATION IS NEGATIVE AND NEGLIGIBLE AS COMPARED TO THE TOTAL CONCENTRATION.

	Series No.	Mgr-mols HCl in 1 grm. solution after use (Phenolphth.) a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Methyl-or.) d	Diff. mols. acid in jelly by Methyl-or. and phenolphth. c—d	Diff. mols. acid in jelly from that in solution absorbed c—ab	Salt "fixed" by 1 grm. dry gelatine
III	1	0.0832	1.57	1.239	0.229	1.108	1.108	+0.784
	2	0.0702	1.52	1.228	0.567	0.661	1.121	—0.064
	3	0.0601	1.3	1.257	0.554	0.703	1.175	+0.354
	4	0.0410	1.64	1.199	0.514	0.685	1.132	—.0329
	5	0.0251	2.05	1.138	0.438	0.700	1.087	—0.545
	6	0.0126	2.05	1.102	0.378	0.724	1.076	—0.762
		Salt in original solutions 3.02 mol. per gram.						
VII	1	0.1796	1.54	1.508	0.592	0.916	1.232	—0.912
	2	0.1492	1.58	1.434	0.548	0.886	1.198	—0.853
	3	0.1184	1.52	1.381	0.565	0.816	1.201	—0.885
	4	0.0872	1.60	1.303	0.665	0.638	1.163	—0.620
	5	0.0717	1.58	1.287	0.539	0.748	1.174	—0.495
	6	0.0564	1.58	1.248	0.414	0.861	1.159	—0.731
	7	0.0409	1.50	1.225	0.420	0.805	1.164	—0.690
	8	0.0262	1.50	1.179	0.288	0.891	1.140	—0.629
	9	0.0100	1.57	1.118	0.259	0.839	1.102	.....
	10	0.0021	1.62	1.095	0.209	0.886	1.091	—0.735
	11	0.0002	3.16	0.728	.....	0.727	0.727	—0.516
	12	.....	15.78	*0.109	.....	0.109	0.109	+0.180
		Salt in original solutions 302 mol. per gram.						
VIII	1	0.1817	13.62	3.495	2.673	0.822	1.020	.....
	2	0.1465	12.98	3.028	1.977	1.051	1.127	.....
	3	0.1154	12.57	2.553	1.558	0.995	1.102	.....
	4	0.0861	11.63	2.088	1.093	0.995	1.087	.....
	5	0.0722	10.93	1.842	0.855	0.987	1.052	.....
	6	0.0570	11.73	1.698	0.871	0.827	1.029	.....
	7	0.0347	11.52	1.426	0.508	0.918	1.026	.....
	8	0.0247	10.99	1.295	0.465	0.830	1.024	.....
	9	0.0096	10.73	1.142	0.221	0.921	1.039	.....
	10	0.0023	9.81	1.010	0.147	0.863	0.987	.....
	11	0.0002	10.44	0.684	.....	0.684	0.682	.....
	12	.....	11.90	0.103	.....	0.103	0.103	.....
		Salt in original solutions 0.76 mol. per gram.						

*This acidity is original acidity of gelatine, due principally to bisulphates.

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Comparing the results with those of Tables 3-5 which give the results with hydrochloric acid alone, it will be noted that the total acid absorbed by 1 gram gelatine is lower, the contraction of volume caused by the salt expelling acid as well as water; but on the other hand the acid "fixed," as calculated by deducting from the total absorbed acid that contained in a volume of solution equal to that absorbed is in all cases higher than with hydrochloric acid alone. This does not necessarily imply that the acid actually attracted by the gelatine is greater when salt is present, but that the dissociation or hydrolyzation is less; or on the other hand, that the obviously doubtful assumption that the concentration in acid of the absorbed solution is equal to that of the external is incorrect. If, as is probable, the concentration of the absorbed solution is really less, the apparent "fixed" acid will increase in some inverse ratio to the volume of the solution absorbed.

On the other hand it must be noticed that the less ionized

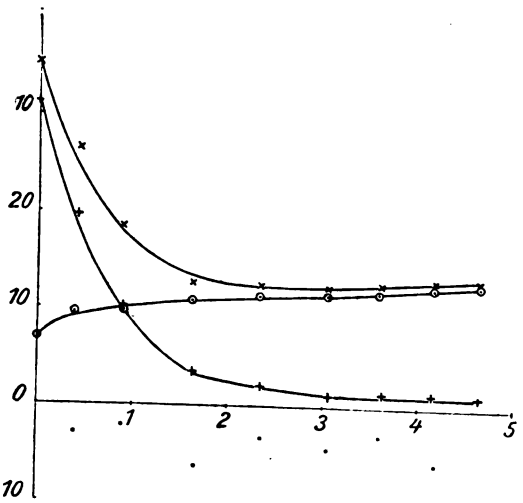

Fig. 3. (Table 12.)—Abscissas; Mgr. molecules NaCl in 1 gr. solution. Ordinates; x = Mgr-mol. HCl in 1 gr. dry gelatine; o = concentration of acid fixed by 1 gr. dry gelatine; + = wt. of solution absorbed by 1 gr. dry gelatine; o = "fixed" salt.

acid, as determined by its non-effect on the methyl-orange, is proportionately, and even actually less in the salted, than in the merely acid solutions. It is, however, by no means probable that methyl-orange is wholly insensitive to the acidity of the

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acid-gelatine, and, unless this is the case, the effect of the latter will be increased by its greater concentration in the contracted jelly, just as methyl-orange is reddened by many organic acids in concentrated solution which scarcely affect it when dilute. Any direct action of the acid gelatine on methyl-orange will diminish its apparent "fixed acid" as determined by this means.

An interesting point in Tables 12 and 13 is that of the amount of salt "fixed," which in presence of hydrochloric acid appears to be always negative, the few apparent exceptions being obviously due to experimental errors, and accompanied by abnormal figures in one or other of the remaining determinations; while Table 11 shows that in absence of acid, a varying

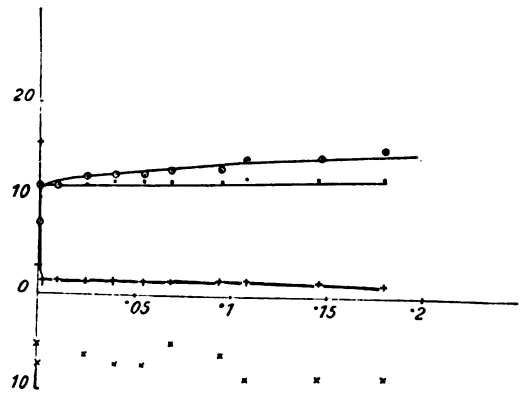

Fig. 4 (Table 13, series VII).—Abscissas; Mgr-mol. HCl in 1 gram solution. Ordinates; . =Mgr-mol. HCl in 1 gr dry gelatine; +=wt. of solution absorbed by 1 gr dry gelatine (b) o = "fixed" acid ; x = "fixed" salt.

positive amount is "fixed." The quantities were calculated by determining the total chlorine in the treated gelatine with argentic nitrate and potassium chromate, and subtracting from this the hydrochloric acid found acidimetrically, and the total chlorine calculated in the solution absorbed. From the large total amount of chlorides present, and the proportionately large effect of the absorbed solution, great quantitative accuracy cannot be claimed for these figures, but they strongly support the view that the chlorine absorbed as hydrochloric acid by the gelatine exerts a corresponding expulsive effect on the chlorine ions (both acid and salt) contained in the solution. It is noted in connection with the experimental work, that in several cases where large

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quantities of salt were used, the sheets of gelatine, instead of appearing homogeneous and transparent, became white and opaque; and this must have been due either to the actual crystallization of salt in the gelatine, or to the formation of a cellular or at least heterogeneous structure enclosing solution of a different refractive index to that of the surrounding jelly. It is extremely probable that this circumstance may account for the irregularity of the figures with regard to fixation of salt.

From the curves given in Fig. 3 it will be seen that the swelling diminishes in a curve of hyperbolic character with increasing concentration of salt, becoming asymptotic to a value apparently somewhat above zero.

Apparently any acid and its corresponding neutral salt will produce a dehydrating effect on swollen gelatine, varying in intensity with the electrolytic dissociation-constant of the acid, and increasing with the concentration of the salt. The effect of sodium sulphate with sulphuric acid appears to be quite as great as that of sodium chloride and hydrochloric acid in equivalent concentrations, while that of the weak acids with their own neutral

TABLE 14.—SULPHURIC ACID AND SODIUM SULPHATE.

Series No.		½ mols. H_2SO_4 in residual solution (Phenolphth.) a	½ mols. Na_2SO_4 in original solution	Wt. of solution absorbed by 1 grm. dry gelatine b	½ mols. H_2SO_4 in 1 grm. dry gelatine after swelling (Phenolphth.) c	Excess over acid calculated in absorbed solution c−ab
XVIII	1	0.05342	0.8173	7.072	1.573	1.195
	2	0.05446	0.6963	9.840	1.629	1.093
	3	0.05668	0.5698	12.75	1.872	1.149
	4	0.05773	0.4374	14.42	1.901	1.068
	5	0.05883	0.2986	15.44	1.992	1.084
	6	0.06053	0.1530	35.18	3.033	0.903

salts is much less, though distinctly marked when compared to the swelling action of the acids alone, as will be obvious in comparing Tables 15 and 16 with 6 and 8. With the weaker acids, the excess of acid absorbed in excess of that due to absorbed solution ("apparent fixed acid") is much less and very irregular as compared to that observed with the stronger acids; and this is particularly the case with the feebly ionized acetic acid,

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of which the ionization is still further reduced by the presence of its neutral salt.

TABLE 15.—GELATINE, FORMIC ACID AND SODIUM FORMATE. SODIUM FORMATE IN SOLUTION 1.33 MOLS.

Series	No.	Mgr-mols. acid in 1 grm. sol. a	Wt. of solution absorbed by 1 grm. b	Mols. acid in jelly of 1 grm. c	Excess over acid in absorbed sol. c—ab
D	1	0.9008	19.45	18.39	0.87
	2	0.4955	17.14	9.11	0.62
	3	0.2049	15.53	3.79	0.61
	4	0.1053	16.04	2.15	0.46
	5	0.0824	16.99	1.71	0.31
	6	0.0574	15.57	1.23	0.34
	7	0.0265	17.07	0.70	0.25
	8	0.0172	15.93	0.44	0.17

TABLE 16.—GELATINE, ACETIC ACID AND SODIUM ACETATE. SODIUM ACETATE IN SOLUTION, 1.33 MOLS.

		Mgr-mols. acid in 1 grm. sol. a	Wt. of solution absorbed by 1 grm. b	Mols. acid in jelly of 1 grm. c	Excess over acid in absorbed sol. c—ab
B	1	0.9656	20.83	20.64	0.50
	2	0.5018	17.64	9.74	0.89
	3	0.1991	15.89	3.32	0.16
	4	0.1007	14.38	1.56	0.11
	5	0.0788	14.20	1.e6	0.14
	6	0.0526	13.20	0.79	0.10
	7	0.0242	12.26	0.39	0.09
	8	0.0143	11.05	0.18	0.02

It is not necessary in order to produce contraction of swelling that the salt employed should have the same anion as the acid, and if the salt is one of a strong acid and in sufficient concentration, good contraction may be obtained even by acidification with very weak acids. Thus effective pickling may be obtained with formic or acetic acid in presence of common salt; and at the writer's suggestion formic acid has been to some extent used commercially for sheepskins, as the antiseptic effect is even greater than that of the customary sulphuric acid, while certain injurious effects of the latter on the final manufactured product are avoided. In the ordinary commercial process, as has been stated, sulphuric acid and common salt are employed; but except for questions of cost, hydrochloric acid and sodium sulphate would be equally effective, as shown in Table 17. Table

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TABLE 17.—GELATINE, HYDROCHLORIC ACID, AND SODIUM SULPHATE.

Series No.		Mgr-mols. acid per grm. Original solution	½ mgr-mols. Na_2SO_4 per grm. Original solution	Mgr-mols. acid in solution after use (Phenolphth.) a	Wt. of sol. absorbed by 1 grm. dry gelatine b	Mgr-mols. acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab
XII	1	0.0574	0.8172	0.0560	7.41	1.492	1.067
	2	0.0587	0.6963	0.0524	8.79	1.457	0.941
	3	0.0601	0.5698	0.0533	8.07	1.513	1.028
	4	0.0615	0.4374	0.0558	9.24	1.603	1.035
	5	0.0630	0.2986	0.0555	10.03	1.682	1.050
	6	0.0645	0.1530	0.0565	11.85	1.766	0.937

Original concentration of acid in water only 0.0663 mols.

TABLE 18.—GELATINE, ACETIC ACID AND SALT.

Series No.		Mgr-mols. acid per grm. Original solution	Mgr mols. NaCl per grm. Original solution	Mgr-mols acid in solution after use (Phenolphth.) a	Wt. of sol. absorbed by 1 grm. dry gelatine b	Mgr mols acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab
IX	1	0.0696	4.373	0.0665	1.37	1.166	1.078
	2	0.0793	2.371	0.0739	2.65	1.217	1.021
	3	0.0874	0.871	0.0839	10.49	1.798	0.918

Original concentration of acid in water only 0.0926 mols.

TABLE 19.—GELATINE, HYDROCHLORIC ACID AND POTASSIUM CHLORIDE.

Series No.		Mgr-mols. acid per grm. Original solution	Mgr-mols. KCl per grm. Original solution	Mgr-mols. acid in solution after use (Phenolphth.) a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. acid absorbed by 1 grm. dry gelatine c	Acid "fixed" by 1 grm. dry gelatine c—ab
XIII	1	0.0551	2.233	0.0524	2.130	1.186	1.069
	2	0.0567	1.914	0.0477	2.677	1.207	1.080
	3	0.0584	1.576	0.0539	3.732	1.263	1.063
	4	0.0601	1.218	0.0555	5.685	1.360	1.044
	5	0.0620	0.837	0.0572	11.19	1.664	1.024
	6	0.0640	0.432	0.0592	12.26	1.746	1.020

Original concentration of acid in water only 0.0663.

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18 shows results with acetic acid and common salt. It will be observed that both the dehydration and the acid "fixed" are practically the same with acetic acid as they would have been if hydrochloric acid had been used.

Table 19 gives a series in which potassium chloride is substituted for sodium chloride with hydrochloric acid. The results are again practically identical with those of sodium chloride.

Summary.

Gelatine absorbs water with evolution of heat, and is capable of exerting large external pressures in the initial stages, but as the quantity of water becomes greater the avidity of the gelatine becomes less, and there is no further perceptible evolution of heat, while the mechanical force exerted is exceedingly slight and may be measured in a few dynes per sq. cm. The process is completely reversible, and water may easily be expelled from the fully swollen jelly by mechanical pressure, and completely removed by evaporation *in vacuo*, and to a large extent by dehydrating agents, though as dryness is approached the last portions of water are removed with great difficulty. The swelling does not proceed to infinity in cold water, but reaches a definite maximum, which is an equilibrium between the affinity for water and the elastic cohesive forces of the gelatine which are influenced not only by its chemical character but by its original volume at setting. In hot water complete solution takes place.

Gelatine is insoluble in, and water-swollen gelatine is impermeable to strong alcohol, which dehydrates and compresses it. If, however, alcohol is incorporated in the liquid jelly which is subsequently allowed to set, and immersed in water, the swelling is increased beyond the ordinary maximum.

Gelatine swells in very dilute acids to a much larger extent than in water. In weak acids this swelling increases with the concentration of acid till finally solution takes place, but with strong acids the swelling reaches a maximum at very low dilutions and subsequently diminishes in a curve of hyperbolic character till the jelly dissolves without further swelling, which limits the possible range of experiment. If, however, a neutral salt of the acid be added, the dehydration may be carried with

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strong acids to a point at which the gelatine forms a solid and horny mass. With weak acids and their salts the effect is less marked but quite obvious. If, however, a weak acid is used with large excess of a salt of a strong acid, the gelatine behaves as if the strong acid only was present, while gelatine swollen with a strong acid and treated with the salt of a weak one naturally behaves as if the weak acid had been used.

In all cases the acid absorbed by the swelling gelatine is in excess of that due to the absorbed solution, and this excess is in any one series of experiments of an approximately constant amount over a wide range of concentration of the acid or acid and salt solution; while under no conditions does it pass a maximum of about 1.25 mgr-mols. of acid per gram of dry gelatine. In the case of strong acids which affect the color of methyl-orange even at very great dilutions, it is shown that a portion of the acid absorbed by gelatine, which varies with the conditions of the experiment but always falls within the limit above stated, has become so considerably less ionized than the free acid that it is incapable of affecting the color of methyl-orange, though it may still be estimated by phenolphthalein.

In the case of common salt it is shown that while in neutral solutions it increases the swelling of gelatine and an amount is absorbed in excess of that normally contained in the absorbed solution, in presence of even small quantities of hydrochloric acid, great dehydration is produced, and the fixation of salt is negative.

Theoretical.

As regards the explanation of the foregoing experimental results, anything which can yet be said, must, in view of the preliminary character of the investigation and the somewhat rough methods of experiments, be regarded as merely working hypothesis. As a preliminary to this, it is necessary to have some definite conception of the actual structure of a gelatine jelly, and the view which is here adopted is that of a network of gelatine molecules cohering to each other, but leaving interstices of molecular dimensions containing water or aqueous solutions, which being within the range of molecular attractions, are really semi-solid solutions in the gelatine, and have with it a common

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internal pressure. The gelatine molecule, consisting as it does, of a complicated chain of amido-acids, is peculiarly fitted to produce such a structure. The range of molecular attraction does not apparently exceed 10 $\mu\mu$ (millionths of a millimeter) and may be much smaller; (cp. Freundlich Kapillarchemie, s 277); but as about 2 per cent. of gelatine is required to form a coherent jelly, there would be in each cubic space of $(10\ \mu\mu)^3$ a weight of gelatine over 13 million times the estimated weight of a hydrogen molecule, and therefore ample molecules for a net of molecular dimensions. The facts mentioned as regards the effect of concentration at the moment of setting on the subsequent swelling give considerable support to the idea of a molecular network formed at the time.

This view, though apparently very similar to the currently accepted one of van Bemmelen and Bütschli, is really very different, since these investigators assume a cellular structure of microscopic dimensions, and hence far beyond the range of molecular forces. That such cellular jellies or pseudo-jellies exist and can be produced is undeniable, but in the writer's opinion it is quite unproved that any such structure naturally exists in aqueous gelatine jellies, the microscopic observations all having been made on jellies hardened and shrunk with dehydrating agents, while no structure could be detected in the unhardened jelly, in which its dimensions if existant, must have been much larger. A dilute gelatine solution which has been sufficiently heated for complete solution shows only stray and probable accidental submicrons, and merely a slight Tyndall effect in the ultramicroscope, so that it is probably, for the most part, a true molecular solution in which the gelatine is uniformly distributed throughout the liquid. On cooling, no flocculation or visible contraction of the gelatine takes place, but the whole solidifies to a transparent and apparently homogeneous jelly, and it is hard to imagine how, under these conditions a cellular structure could be formed. In some other cases, as for instance in the flocculation of albumin solutions by heat, where the gel is obviously less hydrophile than the sol, the network, even if at first uniform and molecular, necessarily contracts, and a reticular structure must result; while when a solution separates into two partially immiscible liquids, an emulsion will be formed, which may be a pseudo-jelly; but

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none of these causes appear to exist with gelatine, and the assumption of a cellular structure does not in any way assist, but considerably complicates the explanation of observed facts.

It is clear that if we accept the conception of a jelly as the solution of a liquid in an elastic solid, the whole question of swelling becomes one of osmotic pressures or perhaps more accurately, one of distribution between two immiscible solvents. In the latter case the common surface takes the place of a semipermeable membrane and as the solvents are no longer identical, the partition-constant (Teilungscoefficient), and sometimes also a different molecular complexity have to be considered. There is also an important difference between the two cases which may be overlooked. In ordinary osmosis the molecular attractions of the common solvent merely serve to overcome and balance those of the solute, and bring it into a region of equal and common internal pressure, where its kinetic energy can exert itself against a fixed semipermeable septum, so that in the terms of gas equation, V is constant and P varies. In the equilibrium of immiscible solvents on the other hand the kinetic energy of the solute is constant, and it is the varying internal attraction of the two solvents for its molecules which determines the partition-constant; and since the diffusion-surface is freely moveable, P is constant and V varies. This latter statement is somewhat modified in the case of jellies by the residual forces of solid cohesion which oppose change of volume. It can be shown, however. that in or near the region of maximum swelling these forces are extremely small. P. von Schroeder[1] showed that a jelly swollen in water lost a large amount of weight and volume (up to 73 per cent.) in an atmosphere of saturated water-vapor, but that this was completely prevented if the jelly were saturated with a N. 10^{-5} solution of an alkaline sulphate, and considerably lessened by one of N. 10^{-6}. It was subsequently shown by the present writer[2] that the energy involved in removing 1 gram water against the osmotic pressure of a N. 10^{-5} sulphate solution (about 350 erg.) was quite comparable to that done against surface tension in forming the surface of a sphere 1 gram weight; and that no doubt the shrinkage might be accounted for in that way. It

[1] *Collegium*, 1903, p. 204.
[2] Brit. Assoc. Rep., 1908, p. 216.

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therefore follows that in most cases of considerable swelling the solid cohesion is almost negligible as compared to osmotic forces. On the other hand in the earlier stages of absorption of water by dry organic colloids, including gelatine, the forces involved are large, as is evidenced by the marked evolution of heat, the contraction of common volume, and the very considerable pressures obtained when the swelling is opposed by mechanical obstacles.

If the swelling of gelatine in pure water be admitted to be osmotic, still more evidently is this the case with regard to the dehydrating action of alcohol on the swollen jelly, since the latter, though freely permeable to water is practically impermeable to alcohol, and the jelly-mass acts as a simple osmotic cell. The curve of swelling in mixtures of water and alcohol (Table 2 is shown in Fig. 1) and is of a simple type corresponding closely to a rectangular hyperbola in the middle portion but diverging at both extremes, possibly because of the solid rigidity of the jelly. There is no reason to doubt complete reversibility. Alcohol shows considerable osmotic pressure in an osmometer with gelatine membrane, and it is shown that alcohol incorporated in jelly must produce a cellular structure, in which the jelly acts as a semipermeable membrane. It is possible that more complete investigation of the dehydrating effects of alcohol on jellies might afford some definite information on their cohesion and osmotic pressures, since the action is purely physical.

The explanation of acid swelling and the peculiar maximum of its curve, and of dehydration of acid gelatine by neutral salts is much more complex, and involves chemical as well as purely osmotic considerations. In what follows the most detailed consideration will be given to the action of hydrochloric acid and sodium chloride, as these have been most fully investigated, and there is no reason to think that the results differ in principle from those of other acids and their corresponding salts.

Gelatine-jelly is known to be very permeable to both acids and salts and to their ions, so that it is not easy to see how either can exert a direct osmotic pressure on the jelly-mass. It has, however, been shown that even very dilute hydrochoric acid is absorbed with some avidity by the jelly, which always contains acid in considerable excess of an equal volume of the surrounding solution with which it is in equilibrium: and this excess, rising

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rapidly at first soon becomes an almost constant quantity (see curve of "fixed acid" in Fig. 2); strongly suggesting the idea of a definite though hydrolyzing chemical compound of the nature of a salt, in which the amphoteric gelatine acts as base. This idea is further supported by the fact that an approximately corresponding quantity of acid becomes neutral to methyl-orange, though it can still be hydrolyzed by sufficient excess of water, and estimated by titration with caustic alkali with phenolphthalein as indicator. If such a gelatine chloride exists, it is extremely probable that it will be much less permeable for hydrochloric acid and other chlorides than the neutral gelatine, or, if we regard the jelly as a solution, that the solubility of salts of a common anion in the acid jelly will be much less than in the neutral, while its affinity for water will be likely to be greater, owing perhaps to its greater ionization. The jelly of course must be in equilibrium with the surrounding solution in every respect, and firstly in regard to hydrolysis, in which it will obey the ordinary law of mass-action. As regards its volume the case is quite analogous to that of solutions of an acid and its salt separated by a movable septum permeable to the acid and to water, but not to the salt, which in the present instance is an indiffusible colloid jelly. The two solutions must be in complete equilibrium, and as the salt cannot diffuse, water and acid must pass through the septum till equilibrium is reached. Firstly then, the common anion must be at equal concentration in both solutions, and because of the salt-anions, the free acid must necessarily be less concentrated in the salt-solution than in that of the pure acid. Secondly the anion of the acid in salt-solution must be in equilibrium with that of the salt itself, and this can only occur by absorption or expulsion of water or acid till the ionic pressure of the salt is equal to that of the acid contained in its solution. Thus, the necessary data being given, the volume of the salt solution or jelly is definitely fixed; and dependent on the concentration of the acid ions, and the ionization and quantity of the salt. Again the quantity of unhydrolyzed and ionizable salt for a fixed quantity of base, depends on the hydrion concentration of the acid and the hydrolysis-constant of the salt; and thus different acids with different constants may produce very varied effects of swelling.

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One consequence of what has just been said must be remarked. It is evident that the "fixed acid" calculated on the assumption that the absorbed solution is of equal acid concentration to the surrounding acid, does not represent the whole of the unhydrolyzed gelatine-salt, but is less than it by the amount of acid expelled by the salt from its solution. Whether the whole of this acid is expelled by the ionized salt, or a part also by the unionized, which demands water for its solution is not easy to determine, but probably unimportant for the general theory of the equilibrium.

It is of course impossible to treat the problem at present in any rigid mathematical way while so many of the factors are unknown, and especially that of the cohesive elasticity of the jelly, but it may be interesting to see how far the experimental results agree with theoretical assumptions.

We have assumed that the combination of gelatine with hydrochloric acid is of the nature of a salt of a weak base with a strong acid, of which the hydrolysis according to Mr. Ostwald is represented by the equation $\frac{hB}{b} = \frac{K_w}{K_g} = k$, when h is the hydrion concentration, b that of (colloid gelatine) ions and B of the hydrolyzed and anionized base (gelatine). K_w is the dissociation constant of water, K_g that of gelatine as a base. It may be taken without serious error that at the dilutions in question, HCl is fully ionized, and that therefore its concentration x in the solution is proportional to h the concentration of the hydrions. b is the concentration of the kation of the ionized but unhydrolyzed salt, and as the quantity of gelatine is constant in the experiment, B is obviously equal to $1-b$. The equation therefore takes the form $\frac{(1-b)x}{b} = k$, and resolving this as regards b, we have $b = \frac{x}{x+k}$ as the measure of the proportion of unhydrolyzed salt.[1] The same expression may also be obtained from the ordinary dilution equation $\frac{a^2}{(1-a)v} = k$, which, substituting the hydrolytic for the dissociation constant, also applies to mod-

[1] The hydrolyzed portion is obviously $\frac{k}{x+k}$.

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erate hydrolysis. In this formula a is the hydrolyzed portion, which above has been called $1-b$; and $1-a$ is the unhydrolyzed salt b while the concentration of the hydrolyzed acid is the same as x, that of the external solution. Substituting these values and resolving as regards b, we again get $b = \frac{x}{x+k}$. It will be observed that v does not appear in this expression, since the concentration is determined by x, and therefore hydrolysis is not affected by the volume of the jelly. The value of b obviously rises rapidly at first and tends to unit value, and the rise is the more rapid and the later part of the curve the more horizontal the smaller the value of k. It must be observed that Ostwald's equation is merely an approximative one, and specially uncertain as complete hydrolysis is approached.

The unit value to which the expression tends is to that of a molecule or equivalent of the salt. In the actual experiments 1 gram of gelatine was used, and neither its molecular weight nor its valency is known, and it is quite possible that the latter may vary since as the acid becomes more concentrated it probably attacks additional amino-groups.[1] It is impossible to calculate equivalent weights from the direct experiments with hydrochloric acid, since much free acid solution is absorbed in swelling, and it has been shown above that this is not of the same concentration as the external solution. In very dilute external acid the error is not considerable, since the total acid of the solution absorbed is small compared to that fixed by the gelatine, but in this case the hydrolysis is also very large. It has been shown, however, that even with the highest concentrations of acid used, the swelling can be reduced to very small proportions by the addition of a sufficient excess of a salt with a common anion (*e.g.* sodium chloride), and as the anion does not increase but depresses the hydrolysis by lessening the ionization of the salt we may safely assume that the hydrolysis in this case is almost nil. Under

[1] It may be noted that both tables 3 and 4 show a sudden and rather considerable rise both in the total acid and in the "fixed" acid (as determined by calculation from the volume of the solution absorbed) at the concentrations above 0.2 N; and though this may be merely due to experimental error, it is more probable that it is an indication that at about this concentration a further amino-group of the gelatine is attacked, corresponding to its increased solubility in the acid.

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these circumstances we find that the total acid absorbed by 1 gram of gelatine is about 1.3 mgr-mols. while that in the absorbed solution does not at most exceed 0.05 mgr-mols. so that we may roughly assume that under the conditions 1,000 mgr. of gelatine combine with 1.28 mgr-mols. of acid, or in other words that the equivalent (though not necessarily the true molecular) weight of the gelatine, considered as mono-valent, is about 780. It will therefore be necessary to multiply the values of x by 1.28 to obtain the actual acid combined with the gelatine-base.

We may now consider the further question of how the volume of swelling is connected with the absorption of acid. The experimental curve is a very peculiar one with a marked maximum, indicating that at first the swelling increases rapidly with increased concentration, but afterwards diminishes inversely in a slower ratio. According to the theory which has been suggested, the swelling is due to the superior solubility or attraction for water of the ionizing gelatine chloride as compared to the non-ionizing neutral gelatine, and it should therefore increase directly with the increase of the chloride. On the other hand it is repressed by the anion of the acid solution, which not merely causes the concentration of the jelly with expulsion of water till its total ionic pressure is equal to that of the acid, but also compels the expulsion of free acid from the jelly against the same pressure of x, so that the total anion-pressure of the jelly-mass may remain equal to x. The force required to compress the jelly therefore varies not merely as x but as x^2, and for a given increment of x the swelling should diminish as $1 - \bar{x}$. We should expect therefore that swelling would be represented by such an expression as $\beta \frac{x}{x+k} \div 1 - \bar{x}$, or $\beta \frac{1-\bar{x}}{x+k}$ where x and k have the same values as before, and β is an empirical constant connecting the volume of the jelly with its pressure. Such an expression will obviously give a marked maximum for some small value of x, and by differentiation it is shown that this maximum occurs when $x = k$. We have thus a means of arriving at a value for k, since the experimental maximum is clearly marked at about $x =$ N. 0.005, and the swelling curve on Fig. 2 is therefore calculated as $7.8 \frac{1-\bar{x}}{x+k}$. It is possible that the true value

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of k is somewhat less than N. — 0.005, and that the higher maximum which this would cause is prevented by the cohesion of the jelly; and since the curve rises much more abruptly than it falls, the effect of this rounding off of its summit would be to shift the apparent maximum to a slightly higher concentration, but in any case if the hypothesis be correct it cannot be much lower than 0.005; and at least the order of the quantity remains unchanged.

Since $k = \frac{K_w}{K_g}$, and K_w is known, we can calculate an approximate value for K_g, the dissociation constant of neutral gelatine, as $\frac{0.6 + 10^{-14}}{0.5 + 10^{-2}}$, or of the order of 1×10^{-13}. It would be interesting to confirm this by more direct measurement.

Of the direct experimental results, only the value of the total absorbed acid remains to be calculated. This is evidently (from the mode of calculation of the "fixed acid"), the sum of the latter and of the volume of absorbed liquid in the jelly multiplied by the concentration of the external solution. As the former approximates closely to 0.8 mols. from the maximum of swelling onwards, and the latter to $x \frac{7.8\sqrt{x}}{x + k}$, the curve has been plotted on the sum of these, and sufficiently well expresses the experimental values, but offers no explanation of the amount and constancy of the fixed acid; a question which is discussed in the next paragraph. It is, however, interesting to note that the curve of absorbed acid is also well represented by $y = 87\, x^{0.41}$, the logarithmic plotting of the smoothed curve being only slightly convex to the origin, and showing that curves quite of the adsorption type may arise as the sum of purely chemical actions.

It has been assumed that the resistance of the jelly to compression by the acid of the outer solution is the product of the direct ionic pressure of the gelatine salt, and of that of the anion of the acid which is expelled along with the water, to maintain equilibrium, but which must carry with it its corresponding hydrion. The swelling pressure within the jelly is thus the sum of three partial pressures of which only one is that of the anion itself and the acid expelled is therefore only one third of

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the total ionized gelatine salt. Since between $x = 0.5$ and $x = 0.3$ the quantity of gelatine chloride and its ionization remain sensibly total and constant, and what change takes place in the one is partially compensated by the corresponding change in the other, the "apparent fixed" and the expelled acid will also remain constant; the one being about 0.8 and the other about 0.4 mols. We have as yet no definite information as to the ionization of the gelatine salt, the repression of which is no doubt negligible within the limits named, but must become considerable in the presence of much sodium chloride or other salt with a common anion. In this case the acid fixed as unionized gelatine salt will increase, and that expelled will diminish, so that the curve of fixed acid must more and more closely approach that of the unionized gelatine salt, as under these circumstances it is experimentally shown to do.

A point much more difficult of explanation is the almost vertical rise of the fixed acid curve near the origin, and its slight maximum corresponding to that of the swelling curve. It is obvious that the really combined acid cannot exceed that of a correct hydrolysis curve, and no constants or modifications can be adopted for the latter to make its rise more rapid which do not at the same time throw the swelling curve derived from it entirely out of harmony with experiment. It is perhaps a somewhat forced, though not I think an altogether improbable explanation, that the uncombined gelatine at first adsorbs acid without actual combination, and that this adsorption is favored by the large volume of the jelly at the point of maximum swelling, where the small maximum also occurs on the fixed acid curve. This adsorption would of course tend to increase the apparent fixation of acid, and render it more uniform, and would disappear with the disappearance of free base, since it is improbable that the chloride would adsorb hydrochloric acid. Some alternative explanations may be suggested, but it is better to wait the results of further experiment.

It must, I think, be admitted that the complicated system of curves which has been deduced from the theory of actual chemical combination shows an agreement with experimental results which is more than accidental, and which in some sense really represents facts, whether these be strictly chemical or not. It

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is not to be denied that an equally plausible hypothesis might conceivably be based on physical adsorption, but to be satisfactory it must show a correlation of experimental facts at least as complete as that which has been offered. It is to be admitted that much remains to be done in explaining the still outstanding deviations, in adducing further proof, and in replacing empirical constants by those based on definite knowledge, but the present paper at least provides a working hypothesis. The most marked deviation of fact from theory consists in the more rapid rise of the "fixed acid" to a small maximum above that allowed by the curve of unhydrolyzed salt, and disregarding probable imperfections in the dilution equation in such an extreme case, it is suggested that this may be explained by actual adsorption preliminary to chemical combination.

It is obvious that the theory affords a complete qualitative explanation of the dehydrating effect of common salt solutions and other chlorides on gelatine (including skin and connective tissue) swollen with hydrochloric acid, although our knowledge of the laws of concentrated solution is insufficient to enable us to apply the same equations quantitatively. The theory asserts that the falling of the swelling is due to the pressure of the chlorine ions, and it is indifferent whether these are furnished by the acid or some other chloride. That salt not only exerts a compressing pressure on the chloride jelly, but is expelled by the latter from the absorbed solution is proved by the last column in Tables 12 and 13 in which the fixation of salt is shown to be negative; though in presence of so much salt, the chlorine estimations cannot claim the same degree of accuracy as the acid ones. That salt exercises no compressing but rather a swelling influence on neutral gelatines is shown by Table 11, in which also the salt absorption is positive. The effect of salt in raising the apparent acid "fixed" is also easy of explanation, since the presence of the chlorine ion limits hydrolysis by repressing ionization, and increasing unionized chloride, and prevents expulsion of acid from the absorbed solution by being itself expelled in its place. A question arises, however, as to whether the compression of the jelly under these circumstances should be treated merely as a case of ionic equilibrium, or not rather as a "salting out" in which the avidity for water of the different con-

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stituents is more important than their ionic pressure, and in which the unionized as well as the ionized sodium chloride plays its part. Throughout, it has been assumed in the equations that the whole of the gelatine chloride and not merely its ionized or unionized part is effective in the swelling; but obviously if the ionization is comparable to that of most salts, it must be practically total up to concentrations such as were used in the acid experiments.

It remains, however, to be considered whether the theory developed from the study of hydrochloric acid is one of general applicability to all acid swelling of gelatine or gelatinous tissues, or whether it is merely an exceptional case confined perhaps to a few of the stronger acids, since sulphuric acid and sulphates show completely parallel effects. (See Table 14.)

It has been often stated that since a swelling effect was common to all acids of sufficient hydrion concentration, the hydrion must be regarded as the active swelling agent; but this in the light of the present theory must be regarded as only indirectly the case, since the hydrion concentration is the measure of the avidity, and hence of the salt-forming avidity of the acid; and it is quite possible that, as in the case of ammonium salts and many other organic bases, not only the anion but the hydrion enters into the salt. In all cases the anion is the compressing and dehydrating agent; and in the absence of a neutral salt, a maximum with subsequent contraction is produced by the acid itself. This is, however, only obvious in the case of the stronger acids, since the weak acid, although it may produce a gelatine-salt, is so little ionized that its anion cannot reach a sufficient concentration to overcome the pressure of the more ionized gelatine-salt. Thus while sulphuric acid produces a marked maximum, that of formic acid though still obvious is much less distinct, and with acetic and lactic acids none is observable, and the swelling continues to increase with concentration, becoming in the end greater than that produced by the stronger acids, and going on without a break to the final solution of the gelatine. In these cases the apparent "fixed acid" is somewhat variable, sometimes higher and sometimes lower than that of strong acids according to whether the ionic concentration is sufficient to prevent hydrolysis or to attack additional amino-groups.

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It may be objected that sodium or potassium chlorides will produce vigorous dehydration not only with hydrochloric acid, but with any other acid of sufficient hydrion concentration to produce swelling; but a little reflection makes it obvious that any such combination simply leads to a quadruple equilibrium in which each acid is balanced against its own neutral salt. Thus in the case of acetic acid and sodium chloride we have gel-ions acet-ions, and an enormous excess of sodium and chlorine ions, and if we imagine combination we must by the law of mass-action have much gelatine chloride balanced against sodium chloride and little gelatine acetate against sodium acetate. Hence the rule, since the salt is always largely in excess, that with the salt of a strong acid, the dehydrating effect is the same whether the acidification has been by a weak or a strong acid, and vice versa. Acetic or formic acid will produce as effective a pickling with common salt as sulphuric or hydrochloric.

As regards other acids and their salts it has been shown that in all cases depression of swelling is caused by a sufficient addition of the neutral salt, but this is most marked with the salts of the stronger acids, possibly because with weak acids the ionization of the salt added is insufficient to repress that of the gelatine compound itself.

I do not propose in this paper to discuss the complicated effect of the action of salts on the swelling of neutral gelatine which has been specially investigated by Pauli, Hofmeister, von Schroeder and others,[1] but it may be suggested that it is quite conceivable that in many cases a portion of the salt undergoes dissociation or hydrolysis, and that both acid and base combine with the gelatine, and that the compound so formed swells or is compressed by the remaining salt solution according to its concentration. Paessler[2] has shown that sodium acid sulphate is dissociated by hide-substance, only the neutral salt remaining in solution, and it is clearly proved in the case of chromic, ferric and aluminic salts that a similar action takes place in which both acid and base (or a basic salt) are absorbed. This absorption of

[1] Pauli (Paseheles) Pflug. Arch., 71. 336 u. 339 (1898).
Pauli u. Rona, Beitr. z. Chem. Physiol. u. Pathol., **2**, 25-26 (1902).
Hofmeister, Arch. für experim. Pathol. u. Pharmacol. **24**, 424, (1888).
von Schröder, *Collegium*, 1902, p. 306.

[2] Wissenschaftliche Beilage des Ledermarkt, 1901, ii, p. 106.

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base may occur either by combination with opened-up COOH groups, or as complex salts such as are often formed by ammonia with other bases; and some of these may form complex ions which are unrepressed by those of the simple salt in solution.

The subject of alkaline swelling is also left untouched, but it is clear from some preliminary experiments, that in certain respects it differs radically from acid swelling. For instance swelling by sodium hydrate is not at all repressed by sodium chloride but is so by higher concentrations of the hydrate, showing that in this case hydroxyl ions and not the kation Na are the swelling and repressing agents. It is hoped to pursue the question of alkaline swelling.

It is obvious that the facts discussed in the paper have an important bearing on many physiological questions and in this connection a crude attempt made in the early stages of the inquiry to imitate muscular contraction may be worthy of mention. A slender spiral platinum electrode was embedded in a cylinder of jelly which was immersed in a salt solution containing a second electrode. When the gelatine electrode was the anode of a sufficient current to electrolyze the salt, the jelly contracted admirably, but its relaxation by a reverse current was somewhat unsatisfactory owing to the evolution of hydrogen which broke up the gelatine. No doubt with a suitable depolarizer better results might be attained, and it is quite possible that the condensation of the anion by a mere surface potential difference might be sufficient to produce the effect.

Pauli[1] has recently published a paper on albumen in which he supports very similar views to those just expressed, though laying more weight on the hydration of the colloid ion than has been done in the present work. In particular he strongly advocates the molecular as opposed to the cellular or network structure claimed by Bütschli. He also mentions the fact that acid jellies cannot be dehydrated by pure alcohol, which has been confirmed in the present investigation, though it has also been found that with acidified alcohol considerable contraction takes place.

[1] Zeitschrift für Ch. & Ind. der Kolloide 1910, S. 241.

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ABSTRACTS.

The Microscopical Examination of Gambier.[1] By H. BRUMWELL.—The cultivation of the gambier plant and the manufacture of the extract from it are carried on mainly by Chinamen, and the product is frequently adulterated with such materials as clay, leaves, stalk, dung, etc. According to Professor Procter[2] *Nauclea* or *Uncaria Gambir,* a climbing shrub widely cultivated in Singapore, is the source of this extract. The plant grows rapidly, the cropping commences three years after planting and is continued two to four times annually with little regard to fitness of shrubs, the plant being cropped until it has hardly leaves left to support existence. This drastic treatment is sufficient to wear out a plantation in from ten to fifteen years.

Cropping is done with a knife called a *perang,* while a larger knife is used for cutting up the leaves and twigs, which are then placed in a boiler sunk in the ground, and boiled with water until the liquid, which is constantly stirred during the operation with a five-pronged stirrer, becomes syrupy. The leaves are then removed from the liquid and allowed to drain on a tray over the boiler. The coarser matter still remaining in the boiler is removed with an instrument similar to a racquet, and the finer by straining through a perforated cocoanut shell into small tubs, where it is allowed to cool with constant stirring with a wooden bar until the catechin crystallizes. When cold the pasty mass is turned out of the tub, cut into cubes with sides about 1 in. long with a hoop-iron knife and dried; this product is known as "cube-gambier." A common quality called "block gambier," instead of being cut into cubes, is run into large oblong blocks, which are wrapped in matting and exported in a pasty condition.

It will be seen that this article cannot be expected to be very pure, considering the crude method employed. Those who have seen the manufacture of gambier state that sand and dirt are actually shovelled into the material during the process.

The concentration of the liquid in open pans must lead to the loss of tannin and darkening of color by oxidation, and the presence of mineral matter in such large quantities must have a deleterious effect in the tannery, as the mineral matter invariably contains iron.

At a meeting of the International Association of Leather Trades Chemists, in London, in November, 1909, when the question of adulteration of gambier was discussed, it was pointed out that the present method of selling gambier was iniquitous, and that under the terms of sale it was impossible to get any satisfaction from the sellers if the delivery was bad.

Reference to the following tables will give an idea of the analyses of a few normal gambiers, as analyzed in the Leather Department, Leeds University, and which were thought not to be in any way adulterated.

[1] *J. S. C. I.*, 1911, April 29.

[2] Principles of Leather Manufacture, page 277.

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	Cube Gambier			Block Gambier		
	"D" Per cent.	"CBL" Per cent.	"S" Per cent.	"P" Per cent.	"A" Per cent.	"B" Per cent.
Tanning matter. =	42.3	44.8	42.6	39.2	36.3	34.6
Soluble non-tans =	31.8	32.3	32.9	31.9	26.2	24.7
Insoluble ..... =	11.2	9.3	9.8	15.1	10.1	11.0
Water ..... =	14.7	13.6	14.7	13.8	27.4	29.7
Ash ..... =	5.4	4.2	3.7	4.3	4.4	4.5

Generally speaking the insoluble matter of gambier consists of material which is in no way available for the manufacture of leather, and not of "difficultly soluble" matter; if more scientific means were adopted in the production, the insoluble matter might easily be reduced to 3 or 4 per cent. at most, and even this might be available for tanners' purposes, as it would very likely consist of catechin, which is only slightly soluble in cold water, and would probably ultimately become converted into tannins by changes in the tan-yard.

A factory has been started to manufacture gambier extract in Indragiri (Dutch East Indies) on similar lines to those used for other extracts. The leaves are extracted with water, the solid matter is removed by suitable means, and the liquor concentrated in vacuum pans. The resulting extract which is in block form, is of excellent color, free from impurities, and contains about 40 per cent. of tannin.

The non-tans are high, which may be due either to the raw material or to the more complete extraction.

The insoluble matter of ordinary gambier, when examined under the microscope, was found to consist of small particles of leafy matter along with a large quantity of hairs. The hairs exist in the extract in larger proportion than on the leaves themselves, since being so fine they are not so easily removed by the crude method of filtering with the perforated cocoanut shell, as are the coarser pieces of leaf.

The cuticles of the leaf were separated by the method suggested by Dr. Hellon, of Whitehaven, which proved very satisfactory both for the leaves and the insoluble part of the gambier. The method is as follows:—A portion of leaf (about 0.1 grm.) is boiled for ½ minute with about 7 cc. of 5 per cent. sulphuric acid and the clear liquor poured away; the residue is then boiled for ½ minute with 7 cc. of 5 per cent. caustic soda solution and the liquid poured away; the residue is boiled for ½ minute with 7 cc. of nitric acid of sp. gr. 1.2, and the clear liquid poured away; the residue is boiled as before with another portion of nitric acid and during the boiling 0.01 gram of potassium chorate is added from time to time until the substance is absolutely white. The clear liquid is poured away, and the residue washed free from acid with warm water, transferred to the microscope slide, covered, and examined.

After the above treatment the cuticles were dyed in a dilute solution

[1] Abstract, this Journal 1909, page 25.

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of Safranine. This method proves very satisfactory for almost all leaf cuticles and is far better in most cases than the nitric acid method, which is sometimes too severe.

The upper cuticle of the leaf is very similar in appearance to the upper cuticle of *Pistacia lentiscus* (frequently used as an adulterant of sumach) having very distinct cells fairly regularly disposed, and no hairs or stomata. The lower cuticle strongly resembles that of *Colpoon compressa* ("Cape Sumach"); the stomata are large, very distinct, in great profusion, and are devoid of hairs. In the samples of insoluble portions of gambier examined, no leaves were found which appeared to be other than those of genuine gambier.

Sago-flour is frequently added to gambier as an adulterant, and can be detected by adding a drop or two of iodine solution to a small quantity of the gambier on a microscopic slide, covering with a cover glass and examining under the microscope. In mixtures of gambier and sago-flour, mixed specially for testing this method, it has proved quite satisfactory, the starchy matter of the flour being colored deep blue and the cellulose deep brown. On the addition of a drop of sulphuric acid the starch granules swell up and finally burst, the cellulose becoming then quite blue.

Sumac. M. C. LAMB in LEATHER, IV, 111, 193, 225, 241.—Great Britain imports yearly upwards of 12,000 tons of sumac, valued at about £10 per ton. Most of this is from Sicily, and consists of the ground leaves of *Rhus coriaria*. The plant is cultivated, yielding a marketable crop the third year. As the age increases, the percentage of tannin in the leaves rises. An inferior variety is also cultivated, whose leaves are larger and the percentage of tannin lower, the color also being inferior.

The leaves and twigs are dried in the open air. Rainy weather causes loss due to darkened color and to fermentation which changes the tannin into gallic acid. The dried leaves are ground and sifted to remove twigs, etc. The finer portion is then ground a second and a third time, being sifted after each grinding to remove fibrous material. The ground material is then "ventilated," by being blown along a long narrow room by means of a fan. This room is several hundred feet long. Sand and other heavy particles, most of which are from the wear of the mills, drop near the fan.

Sumac is very liable to be adulterated, the most common substances used for the purpose being *Pistacia lentiscus, Tamarix Africana* and *Ailantus glandulosa*. In order to evade the strict Italian laws in regard to adulteration of sumac, many ingenious devices are resorted to. One of these is to ship the pure sumac and adulterants separately and have them mixed and re-bagged on ship-board.

The percentage of tannin in sumac varies from 22 to 30 per cent. All the adulterants are much lower. In the table a good sample of sumac is compared with average values for the three adulterants mentioned:

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	Rhus conaria	Pistacia lentiscus	Tamarix Africana	Ailantus glandulosa
Tannins	26.4	12.8	9.1	11.2
Soluble non-tans	17.6	20.5	25.3	20.4
Insolubles	48.2	58.2	57.6	60.0
Moisture	7.8	8.5	8.0	8.4
Ash	8.8	6.8	10.5	....

The author concurs with S. R. Trotman in the suggestion that as a standard for mineral constituents of sumac the following figures be adopted:—Ash, 6.5 per cent., silica, 0.75 per cent., iron, 0.15 per cent. A total ash of over 8.5 per cent. may be regarded as indicating presence of Tamarix Africana or very bad ventilation.

The common adulterants of sumac may be discovered microscopically. Treatment with nitric acid almost completely destroys sumac leaves, while a certain part of the adulterants is not destroyed and may be filtered out and examined. The sumac leaf has very fine hairs which are absent from both Pistacia and Tamarix. One sample examined by the author was adulterated with spent sumac, dried and reground.

Sumac is one of the most valuable tanning materials for light leathers intended for book-binding, upholstering, etc. Considering the high proportion of available tannin, sumac is a relatively cheap material. The leather is soft and supple, and very light in color, so that it may be dyed in a great variety of shades. It is particularly valuable for book-binding because of its high resistance to gas fumes and other agencies liable to destroy bindings.

The tannin of pure sumac is mainly gallo-tannic acid, that of the adulterants being a catechol tannin. Sumac leather, unlike that made with catechol tannins, is not changed in color by the action of light.

The tannin of sumac is much less astringent than most tannins. so that a strong infusion may be employed even in the early stages of tanning without causing drawn or hardened grain. Sumac tanning is done at a comparatively high temperature, 25° to 30° C., (77° to 86° F.).

Sumac is best extracted at a temperature not exceeding 60° C. (140° F.). As much as one-fourth of the total tannin may be destroyed by extraction with boiling water. The infusion obtained at the higher temperature is also darker in color. The extraction is best done by placing the sumac in cold water, raising the temperature to 60° C. and maintaining that temperature for one hour.

Sumac infusion begins to ferment within two or three hours after it is made, the tannin being rapidly hydrolyzed into gallic acid.

Small black stains often occur on sumac leather, due to minute particles of iron or iron ore from the stones used in grinding the sumac. These may be avoided by letting the liquor settle before the skins are allowed to stand in them. Brown color in sumac leather may be caused by imperfect deliming. Yellow stains may be caused by too high a temperature in the tanning, causing the grease of the skins to combine with the coloring matter of the sumac.

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Leather which has been tanned with other materials may be considerably lightened in color by retannage with sumac. This is done by drumming in a strong infusion of sumac, of a pasty consistency in consequence of solid matter in suspension. These solid particles are forced into the leather, making it firmer and thicker.

All vessels used in extraction or tannage should be steamed before being used again, to kill the germs which cause the gallic fermentation.

Souring of Tan Liquors. R. W. GRIFFITH in *Shoe and Leather Reporter,* March 16, 1911.—Liquors from myrobalans and valonia and from some barks sour naturally, while those made from woods do not to any extent. The souring is due to the fermentation of sugary matters called glucosides, giving a mixture of organic acids. The woods contain less sugar and therefore produce less acid. To increase the acidity of liquors the addition of glucose has been tried, and sometimes with success. An important difficulty is presented by the many undesirable fermentations liable to occur and hard to control. The total amount of acid in the liquors rarely exceeds 0.8 per cent. The bacteria which produce the acids cannot work in the presence of larger proportions of acid.

The direct addition of organic acids to the liquors is now practiced, the advantage of this method being that the souring is thus under complete control.

The hides are often put into the tail liquors in an alkaline condition, due to lime, and the acids must first neutralize the lime before the hide can absorb tannin. In this process the hide falls. The second function of the acids of the tail liquors is to restore the plumpness of the hides, and render them acid so that the tannin can be absorbed. In a yard where the tannin in the tail liquor is about 1 per cent., the acid should be not less than 0.35 per cent. In the head handler, with 3-4 per cent. tannin, the acidity should be about 0.6 per cent. In the layer liquors not much acidity is required.

Hides absorb more non-volatile than volatile acid. Roughly, the volatile acid in a liquor represents its neutralizing power and the non-volatile its plumping power. The absorption of non-volatile acids by the hide also determines to some extent the capacity of the hide for tannin, as it establishes a permanently acid condition in the hide.

The presence of a small quantity of salts in a liquor hinders the plumping effect of acids. (See this JOURNAL, 1908, p. 154.)

One-Bath Chrome Tannage. ALAN A. CLAFLIN, in *Shoe and Leather Reporter,* April 20, 1911.—The writer believes that the one-bath process will supersede the other for all purposes. He gives three reasons, 1st, because actual progress is being made in this direction, 2d, because the one-bath process is capable of more exact scientific adjustment than the other, 3d, because it is cheaper.

The one-bath method is the oldest form of chrome tanning, having been experimented with by Knapp nearly sixty years ago. In a one-bath liquor we have a plumping acid due to the hydrolysis of the chrome

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salt, and two sorts of salts, the chrome salt and the sodium salt due to the neutralization of the acid formed by hydrolysis with sodium carbonate. The chromium salts have much less depleting effect than salts of sodium.

The tanning solution is acid to litmus. As the hide absorbs the tanning agent from the bath, whether this be chromium hydroxide or a basic salt of chromium, the equilibrium between the plumping acid and the depleting salt is upset, and must be restored by additions to the liquor. This restoration is not so important in the case of lighter leathers, because as the tanning progresses the skin becomes less susceptible to the plumping effect of acids and the depleting effect of salts.

With the heavier leathers it will be found that the acid is withdrawn (at least in all solutions that have been examined by the author) faster than the chromium salts are taken up.[1] In order to penetrate the thick hide there must be a certain excess of tanning agent. The author advises strengthening the one-bath liquor with concentrated solutions of chrome salts which are less basic than the original solution.[2]

Analysis of liquors before and after the skins are put in shows that the skins take up from the bath the chromium in the form of a basic salt rather than the hydroxide. On the other hand analysis of the leather does not show the presence of so much inorganic acid in combination with the chromium as to correspond with that taken up from the bath. It seems probable that a certain amount of acid is necessary to take the chromium into the skin, but this is removed in the course of subsequent operations.

How best to prepare a one-bath liquor is also of as much interest as how the liquor acts when it is prepared. The cheapest source of chromium under present market conditions is the bichromate of soda. This salt must be reduced before it can be used for the liquor. The cheapest reducing agent to use is theoretically glucose. To use glucose sufficient acid either muriatic or sulphuric is added to set free chromic acid according to the reaction.

$$Na_2Cr_2O_7 + H_2SO_4 + H_2O = Na_2SO_4 + 2H_2CrO_4$$

or

$$Na_2Cr_2O_7 + 2HCl + H_2O = 2NaCl + 2H_2CrO_4.$$

Then the glucose is added which reduces the chromic acid, chromium sulphate, water, and carbon dioxide being formed.

To translate this into pounds and allow for the percentages of the chemical compounds in the commercial products, *e.g.* commercial glucose contains 30 per cent. water, we find that 2.6 lbs. glucose will reduce theoretical 6 lbs. of bichromate of soda and with 8½ lbs. sulphuric acid form the normal chromium sulphate. The objection to the use of the

[1] The reverse of this statement is true, in some instances at least. ED.

[2] The exact reverse of this is recommended by some writers. See for instance this Journal for March 1911, p. 156.

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glucose is that the reduction practically can never be made to work according to the theoretical reaction. Much of the glucose for instance is lost by volatilization in the form of aldehyde, and so an excess must be used, some of this excess will then also in all probability remain as unchanged glucose, and we have present in our one-bath liquor organic matter which is a complication and in my experience interferes to some extent with the efficiency of the tannage. Therefore for practical purposes it is probably better to use bisulphite of soda for the reducing agent.

For 6 lbs. of bichromate of soda 20 lbs. of bisulphite of soda and 5½ lbs. of sulphuric acid are required to produce the normal sulphate. To convert the normal chromium sulphate into the basic sulphate required for tanning purposes, sodium carbonate should be added according to the following equation:

$$Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2,$$

or in pounds, for the amount of normal sulphate produced from 6 lbs. of bichromate about 2 lbs. of sodium carbonate should be used. With the liquor once prepared the plumping and depleting properties may be regulated by the addition of common salt.

Crucible Support. W. M. THORNTON, JR., in *Journ. Ind. and Eng. Chem.*, May, 1911, p. 343.—The support consists of a slab of soapstone supported on iron legs with 3 inch holes conveniently spaced, adapted to the use of any standard triangles. The soapstone does not rust, and lids may be temporarily set on it, or crucibles left to cool. This apparatus has been in use in the laboratory of the Va. Geological Survey for 2 years with satisfaction.

Estimation of Soluble Mercuric Salts at Great Dilution. PROFS. H. R. PROCTER and A. SEYMOUR-JONES. J. S. C. I., April 15, 1911, p. 404.—In the presence of certain organic acids, such as formic or citric, mercuric sulphide is not precipitated on treatment of the mercuric chloride solution with H_2S, but remains in the colored colloidal form in solution. This color is definite for definite concentrations of the chloride and acid, if the liquid has been saturated with H_2S, and is directly proportional to the concentration of the original chloride solution. In making the comparisons a Schmidt and Haensch dipping colorimeter was used, (described in J. S. C. I., 1910, pp. 663-666, Reprint, this JOURNAL, August, 1910, p. 352).

A standard solution of one part $HgCl_2$ in 10,000 parts water and containing also 1 per cent. (by weight) of formic acid is saturated with H_2S and run into a 1 cm. cell, placed on the upper platform of the colorimeter. This gives the standard color, against which any solution of $HgCl_2$ weaker than 1:10,000 may be matched. The mercuric salt of unknown concentration is then made into a 1 per cent. formic acid solution and saturated with hydrogen sulphide gas. The colloidal sulphide solution is run into the dipping cylinder of the colorimeter, and

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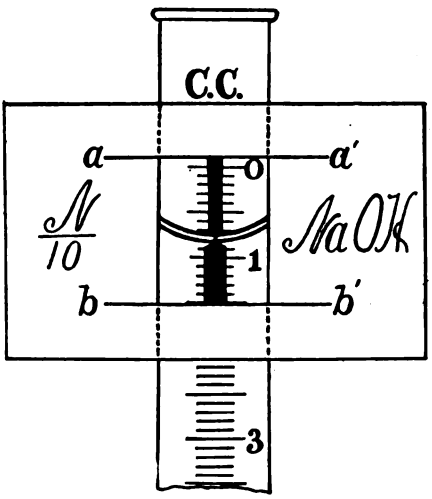
the dipping stage adjusted until the field of view in the telescope is of uniform color. The depth of the solution thus found is read off and its concentration calculated. As the depth of the standard is 10 mm., and its concentration 1 in 10,000, the concentration of the unknown may be easily found. With practice the difference between 76 and 77 parts per 100,000 may be distinguished.

A Simple Help for Reading the Ordinary Burette. Dr. Jaroslav Milbauer. *Chemiker-Zeitung,* 1911, p. 419, April 18.—In many laboratories, especially technical chemical laboratories, a very convenient form of burette, described by Schnellbach, is used. The Schnellbach burette has a white glass background, in the middle of which is a blue line, about 2 mm. wide. With clear liquids, not too dark colored, this line gives a sharp point, as reflected in the surface of the liquid. The level being thus sharply defined, readings may be taken with accuracy, ease and rapidity. For many years the writer has used the same principle in reading the ordinary burette. The apparatus herewith illustrated is



exceedingly simple, consisting preferably of a glazed visiting card, on which a blue or red line 2 mm. wide has been drawn between two slits *a a'* and *b b'*. The effect is quite analogous to the Schnellbach burette. The card must of course be slid up or down the burette as the level of the liquid is changed. The card also serves as a label. L. B.

Essential Qualities of Vegetable Tanning Materials. Dr. J. Paessler in *Shoe and Leather Reporter,* March 16, 1911.—The problem of the economic use of tanning materials is not quite the same in the case of leathers which are sold by measure as in that where they are sold by weight. The following points are to be considered:

[1] *Chem.-Ztg.,* 1885, p. 1482.

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1—Cheapness; 2—Thorough extraction; 3—Liability to deteriorate in the tanning process; 4—Capacity to penetrate or be absorbed in large quantity. In making leathers to be sold by weight, all four points must be considered; in the other case, only the first three.

Prices of some tanning materials in the German market are as follows:

	Per cent. tannin shake method	Price of tannin m. per kilo.	Price of tannin cents per lb.
Oak bark	9.0	1.17	13.3
Oak wood extract	25.0	1.00	11.4
Valonia	27.0	0.93	10.6
Chestnut extract	28.0	0.86	9.8
Pine bark	10.0	0.65	7.4
Quebracho	19.0	0.63	7.2
Dividivi	38.0	0.63	7.2
Mimosa bark	33.0	0.61	7.0
Trillo	40.0	0.60	6.8
Myrobalans	30.0	0.50	5.7
Mangrove bark	38.0	0.39	4.4

The tannin in the extracts being more nearly all available, these prices do not give a fair comparison.

In considering the extraction of tanning materials care must be taken not to confound complete extraction with advantageous extraction. In many cases the more easily extracted and lighter colored tannin is much more valuable for the purpose intended.

The third point, that some liquors change with time, has often been overlooked. Some liquors remain clear, while others thicken badly, and still others separate considerably. Mangrove, mimosa and quebracho remain clear for as much as two months. An oak bark liquor becomes cloudy and one made from myrobalans becomes cloudy and separates considerably. Much of this is due to the tannin passing over into an insoluble form, thereby becoming unavailable. If, however, this change takes place after penetrating the skin, the result is beneficial. The percentages of tannin lost after 60 days for several materials are as follows, for a liquor of 14° Barkometer.

	Per cent. loss of tannin
Mangrove bark	0
Mimosa bark	2
Quebracho wood and extract	3-4
Gambier (cube)	0
Oak bark	5-7
Pine bark	10
Chestnut wood extract	11.5
Oak wood extract	12.5
Myrobalans	24
Valonia	29

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The fourth point, weight giving properties, has been the subject of experiments at the Freiberg Institute. More tannin is absorbed in the presence of acid than in non-acid or feebly acid solutions. The best weight giving materials are quebracho wood, mimosa bark, oak wood extract, chestnut wood extract, oak bark, pine bark, mangrove bark and valonia, in the order named. Cold soluble quebracho extract gave a low weight.

The Estimation of the Saponification Value. L. W. WINKLER. *Zeitschr. f. angew. Chem.*, April 7, 1911, p. 636.—The author recommends the use of propyl alcohol instead of ethyl alcohol for the alcoholic potash solution, because on account of its higher boiling-point it makes possible the more rapid saponification of the material. Beeswax may be completely saponified in 10 minutes. No return condenser is necessary.

Ordinary commercial propyl alcohol is purified by distillation after standing a few days with 1 gram of KOH per liter in solution. In each liter of the redistilled liquid, 30 grams of the purest obtainable KOH is dissolved, and the solution filtered through a small cotton plug. This solution is approximately N/2. The KOH, crushed to a coarse powder, dissolves readily in propyl alcohol, the carbonate remaining undissolved so that it is removed by filtration. The flask being occasionally shaken, solution is complete in a few hours, but filtration is best postponed for two or three days. The solution thus prepared is colorless and after long standing becomes only slightly yellow.

To determine the saponification value, about 2 grams of the fat or wax is weighed into a flask of about 100 cc. capacity, and 25 cc. of the KOH solution run in. The flask is so covered with a small beaker (25 cc.) that the rim of the beaker does not touch the flask, and placed on the steam bath for 10-20 minutes. The heat is so adjusted that the contents of the flask may boil gently and evenly. Then about 0.01 gram of phenolphthalein is placed in the hot liquid and the excess of KOH titrated with N/2 HCl. In the case of materials difficult to saponify the time on the steam-bath is prolonged to 20-30 minutes. A blank determination should always be carried out. The author recommends for introducing the alcoholic potash a pipette furnished with a glass stop-cock and two marks, containing 25 cc. between them.

The author recommends for finding the acid value of oils and fats that 5.6 grams be placed in a glass-stoppered flask of 50 cc. capacity, 20 cc. of neutral alcohol added, with 0.01 gram phenolphthalein and then titrated with N/10 soda. For solid fats and waxes, a smaller quantity may be used, and dissolved in warm propyl alcohol.

A table of results is given, the saponification value of each substance having been taken after 10, 20 and 30 minutes heating. The three results are practically identical except in the case of wool-grease. In this case the value increased up to 30 minutes, but heating for 45 and 60 minutes showed no further increase. The author gives directions for the recovery of the propyl alcohol, stating that a moderate water content does no harm.

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	Acid value	Saponification value
Almond oil	1.2	192.1
Olive oil	2.4	191.1
Sesame oil	6.1	191.0
Poppy oil	2.6	192.8
Rape oil	4.1	174.6
Castor oil	0.8	181.2
Linseed oil	3.1	192.7
Cocoa butter	3.4	194.5
Butter fat	1.2	223.6
Lard	0.0	196.5
Beef tallow	0.1	198.2
Whale oil	0.1	123.2
Wool grease	0.3	93.5
Bees-wax, 1	21.5	92.8
Bees-wax, 2	19.0	92.2
Bees-wax, 3	19.8	93.8
Japan wax	19.0	216.8

Tannins and the Tannery. Oak. U. J. THUAU. *Le Cuir,* 1911, Nos. 1 and 3.—Of all the tannins, those furnished by the oaks are most widely distributed. There are more than three hundred species of oaks. The wood contains tannin, and that of some species is used in making extracts. The bark of the oak is used directly in tanning and was for centuries the only tanning material used. Some species furnish fruits rich in tannin and much used, as valonia and knoppern. Gall nuts also grow on the oak. Finally the bark of the roots and the roots themselves of some species furnish very choice tannin. With the exception of valonia, the use of all forms of oak tanning materials is probably decreasing.

Oak wood is used to some extent in the manufacture of extract, and this industry is not increasing. Oak wood extract is very difficult to decolorize. It has low tannin content and high non-tans. Because of its high content of glucose it tends to ferment. A further reason for the small production of this material is that the yield of extract per cord of oak wood is small. Extract of oak wood, decolorized, is an excellent type of tan-stuff for sole leather because it furnishes a natural plumping effect. The tannin of chestnut wood extract is all of the pyrogallol class, while that from oak wood is a mixture of catechol and pyrogallol tannins. The presence of catechol tannins in the latter gives it great penetrating power.

Nine species of European oaks are mentioned. Of these the bark of *Quercus suber* has the highest percentage of tannin, (19 per cent.), but it is too red to be satisfactory.

The percentage of tannin in both wood and bark is less near the top of the tree than at the base. Old trees yield more tannin than younger ones, and the wood is of a deeper color. The deeper color of the heart wood also corresponds to a greater tannin content. Heart wood from

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the base of an oak 2 feet in diameter gave 6.7 per cent. tannin, sap wood 1.2 per cent. Heart wood from the top of the same tree gave 4.8 per cent. and sap wood 0.9 per cent. From the largest branches, heart wood gave 6.1 per cent. and sap wood 2 per cent. The percentage also varies very much in different trees so that it is very difficult to obtain a dependable average. Heart wood from a tree more than 100 years old gave 9.8 per cent. tannin and 1.1 per cent. non-tannins.

The tannin from old oak wood is quite different from that of the bark. On heating extract of oak wood with bromine water, a characteristic green coloration is obtained at once, while bark extract gives the same coloration only after a considerable time. Means of analyses of oak wood extracts at 25° Beaumé:—

	Good extracts Per cent.	Extracts from young wood Per cent.
Tannin	26.5	16.1
Non-tans	13.0	20.6
Insolubles	0.5	0.9
Water	60.0	62.4
Sugar	3.1	....

Extracts from oak and chestnut woods resemble each other so much that it is difficult to distinguish them without analysis. Oak extract is generally clearer than chestnut, however. A good oak extract ought to dissolve very easily in cold water without much sediment. The yield of extract at 25° Beaumé is only 12 to 15 per cent. of the weight of the wood. Few samples of so-called oak-wood extract found in the market are pure, straight chestnut being often sold as oak.

Oak-wood extract made from liquor extracted without pressure and at a temperature not above 80° C. (176° F.) is one of the best for vat tannage giving a good yellow color and penetrating rapidly. This extract is particularly satisfactory for sole leather because of the firmness which it gives to the product. It is used to advantage mixed with oak bark liquor in the layers.

Beside the fault of lack of purity, oak wood extract has the disadvantage of decomposing easily. The table shows the changes undergone by a liquor made from oak-wood extract during a period of two months. The figures are grams in 200 cc.

	At start	After 6 days	After 18 days	After 1 month	After 2 months
Tannin	2.07	2.05	1.97	1.85	1.71
Non-tans	0.92	0.94	0.91	0.70	0.49
Total solubles	2.99	2.99	2.88	2.55	2.20
Insoluble	0.0	0.0	0.01	0.14	0.22
Total solids	2.99	2.99	2.89	2.69	2.42
Loss of tannin	..	0.7%	3.2%	7.4%	12.0%

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Tannin and non-tans diminished together forming not only insolubles but also volatile matter which evaporated.

Oak bark is the best known tanning material. Three grades are distinguished, depending on the age of the tree. Oak bark, like the wood, is richer in tannin near the base of the tree than near the top. The tannin content varies from 8 per cent. to 15 per cent. averaging about 10 per cent., with a mean water content of 14 per cent. In order not to decompose the tannin during extraction it is best not to exceed a temperature of 80° C., (176° F.). If the extraction is done under pressure, much loss of tannin takes place. A sample which gave 11.1 per cent. tannin with boiling water, when extracted under a pressure of two atmospheres, raising the temperature to 122° C. (152° F.) gave only 8 per cent. At 4 atmospheres, (146° C., 295° F.) the amount was but 5.6 per cent., and at 6 atmospheres, (160° C., 420° F.), but 3.2 per cent.

For a long time it was believed that oak tannin was simple, and it was called quercitannic acid, and was classed as a catechol tannin. Stiasny's method of separating pyrogallic from catechol tannins by precipitation of the former with formaldehyde and hydrochloric acid, proves clearly that both kinds are present in oak bark. It would be interesting to determine the percentage of each, and what proportion of each is extracted at different temperatures. If colorless soluble tannin from oak bark be heated in a closed glass tube with water at 100° C., it changes into a red brown substance, difficultly soluble, and which is identical with the coloring matter found in oak bark. This change takes place with separation of water, and the product is a difficultly soluble phlobaphene.

Some recent experiments seem to show that at a low temperature, nearly all of the pyrogallic tannin of oak bark is capable of extraction but only a part of the catechol, the remaining parts of the catechol requiring a higher temperature. That portion requiring a temperature about 80° C. is dark colored, due to partial conversion of tannin into phlobaphenes.

The phlobaphenes of oak are very little soluble in water and deposit from it easily, but they are more soluble in solutions of oak tannins extracted below 50° C., (122° F.). It is advisable to let oak liquor stand to deposit the coloring matters or phlobaphenes, or even to filter it. It would be of advantage also not to mix the liquor extracted below 50° C. with that extracted from 50° to 80° C. The latter will on standing deposit a much larger quantity of coloring matter than the former, and the total quantity deposited will be greater than if they were mixed before standing, on account of the greater solubility of the coloring matters or phlobaphenes in the liquor extracted at a low temperature.

L. B.

Lactic Acid Anhydrides. DR. A. A. BESSON in *Chemiker Zeitung*, 1911, p. 26.—The author published in *Collegium* in Feb., 1910, an article on "'Lactic Acids and their Anhydrides." (Abstract, this JOURNAL, 1910,

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page 231.) In this article he called attention to the fact that researches were in progress to determine the nature of the impurities which prevent correct results when the crude acid is heated with KOH. This research is still incomplete, and the present article is called out by Leon Monin's publication (Rev. gen. mat. color., 1910, vol. 14, p. 279) of a method of analysis. Monin claims that the commercial lactic acid cannot contain lactic anhydrides. His method is as follows:—Shake 2 grams commercial lactic acid with 30 cc. absolute neutral alcohol. Let stand, filter, wash with ether and evaporate in vacuum. Take up the residue with boiling water and titrate with soda and phenolphthalein.

Besson says that this method takes much time and does not give correct results. The author's method involves permitting the acid to stand some time with an excess of alkali without boiling, and then titrating the excess of alkali with standard acid. This method gives higher results than Monin's, particularly with concentrated solutions, and the author claims that this is due to the slow taking up of anhydrides by the alkali. A sample of lactic acid made by decomposing C. P. calcium lactate with H_2SO_4 which showed 18.01 per cent. free acid was treated by Besson's method and gave 18.01 per cent. combined acid. This same solution was concentrated in vacuum so as to show 78.45 per cent. free acid, when the combined acid shown by Besson's method rose to 84.89 per cent., indicating 6.39 per cent. present as anhydride. L. B.

The Testing of Tannin Extracts. A. GANSSER. *Collegium,* 1910, 101-6, 109-113.—The author describes further applications of his "animalized cotton" prepared by coating cotton with gelatine treated with formaldehyde. While not giving absolute values, this testing material is regarded as giving useful relative numbers for comparing extracts and it has the advantage over hide in being uniform.

Determination of Properties Giving Weight.—The percentages of increased weight of four different materials treated with various extracts were:

Extract	Silk	Hide powder	Grain split cowskin	Animalized cotton
(1) Quebracho, "Triumph"		35.0	41	16.2
(2) Quebracho, "Filling Ext." ..	25.0	37.1	45	11.5
(3) Quebracho, DDBM	27.2	28.5	34	15.3
(4) Chestnut, I	22.1	22.9	..	16.46
(5) Chestnut, F	22.1	38.5	..	19.05
(6) Mimosa, DC.		34.0	..	15.9

In using the cotton, 3 to 6 pieces are taken (2.5 grms. each) with 4 times that amount of liquor of 6° B. and tanned 12 hours, then dried directly, finishing at 80-90° in vacuo.

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While the other materials gave variations of 10 per cent. in duplicate tests, the "animalized" cotton gave more concordant results :

Extract	Per cent. tannin	—Gain in weight, test—	
1.	35	24.1	25.4
2.	10-20	17.4	17.4
3.	37	19.6	21.4
4.	29	14.9	14.3
6.	37	21.7	22.3
7.	31	20.6	20.6

As the treated cotton is hygroscopic (8-10 per cent. gain in 12 hours) the air dried product is preferred to the desiccated preparation.

Determination of Properties Giving Strength.—Longitudinal test strips 50 × 16 cm. were tanned as before, then trimmed to 30 × 5 cm. and tested with a dynamometer, giving comparative breaking strengths. The original test material gave: plain cotton 15.51, "animalized" cotton 17.74. A blank test with pure water corresponding to the tanning conditions, gave 15.06 showing a loss of strength due to softening and solution. After tanning with various extracts and correcting for above loss, the following increases were found; chestnut (clarified) 1.28 chestnut, (blood decolorized) 3.28, American hemlock 1.66, European pine 2.09, sumac —0.65, myrobalans 0.88, quebracho 1.28, Kaki cutch 2.17, Indragiri gambier 2.0, quebracho sulphited (Lepetit) 2.8. Tests made upon mixtures gave results agreeing well with figures computed from above. It is thought that by further research, fairly reliable numbers may be obtained which will characterize the type of extract. Parallel trials with split hide gave much less uniform results.

Determination of Water Solubles in Leather. LOTHAR GODEL. *Collegium,* 1911, 113-4.—The author has observed that rasped leather gives higher solubles than the ordinary milled sample; with the latter, a tannage number of over 100 was sometimes obtained. He prefers to pulverize the leather with an ordinary coarse wood rasp and extract 12-15 grams in a cylindrical separatory funnel of 150-200 cc., which permits of occasional stirring; 4-5 hours are required.

Methodic Tannage of Goat and Sheep Skins in the Drum. *Le Marché des Cuirs,* 1911 [23] 74-5.—The tannage, with sumac for example, should be progressive, beginning with weak, finishing with strong liquors; the residual liquors are used progressively to exhaust their tannin. Chemical analysis of the liquors gives a better control than gravity determination and when made once for all, rules for practice are established. Four liquors are used for strengths ¼, ½, ¾ and 1, the hides remaining in each one day.

PATENTS.

Reconstructed Leather. U. S. Patent No. 989,788. MATTHEW MASON, New York, N. Y., assignor to the Arlington Leather Company.

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The process involves mixing leather and balata gum and subjecting the mixture to pressure.

Evaporator. U. S. Patent 989,982. PAUL KESTNER, Lille, France.

Evaporator. U. S. Patent No. 989,996. JOHN PARKER, Philadelphia, Pa.

Evaporating Apparatus. U. S. Patent No. 990,878. JOHN E. KAUFFMAN, Kansas City, Kansas.

Feed-Regulating Device for Evaporators. U. S. Patent No. 991,342. RALPH MELLOR, Philadelphia, Pa.

Leather Working Machine. FRANKLIN JAY PERKINS, Woburn, Mass., assignor to the Turner Tanning Machine Co.

Vacuum Evaporator or Heater. U. S. Patent, reissue No. 13,425. JOSEPH E. DUNN, Philadelphia, Pa.

Process of Producing Carbon Tetrachlorid. U. S. Patent No. 992,551. WILLIAM F. DOERFLINGER, New York, N. Y.

Hide-working Machine. U. S. Patent No. 993,068. ALBERT A. HUTCHINSON, Winchester, Mass.

Composition for Waterproofing and Preserving Leather. U. S. Patent No. 993,315. CHARLES L. MILLER, Lynn, Mass.

The materials used are pine tar, linseed oil, Japan, and blue vitriol.

Method of Treating Leather. U. S. Patent No. 993,438. ELMER V. CUSHMAN and HARRY WRIGHT, Canton, Mass.

The materials used are linseed oil, bees-wax, indulin, stearic acid, and paraffin.

Process for the Manufacture of an Elastic Caoutchouc-like Substance from Animal Matter. U. S. Patent No. 993,626. WILLEM VAN DER HEYDEN, Amsterdam, Netherlands.

The process consists in boiling such materials as fish, mollusks and the mucous membranes of the intestines of mammals, filtering off the broth, evaporating it down, adding sulphur or sulphur and caoutchouc and vulcanizing it.

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Journal of the

American Leather Chemists Association

Vol. VI JULY, 1911 No. 7

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Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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THE TREATMENT OF TANNERY EFFLUENTS.

By J. A. S. Morrison.

With the growth of manufacturing industries in the early part of the Nineteenth Century came the attendant evils of river pollution. The most natural sites for new and progressing industries were on the banks of streams, for our forefathers were quick to recognize the advantages of situation. As can be imagined the increasing pollution consequent upon increasing prosperity of trade gradually attained such dimensions as seriously to affect the public health. The natural result was that communities quickly demanded means for the prevention of what was undoubtedly a public scandal. Repeated complaints and official inquiries led to the appointment of Royal Commissions and subsequent legislation. Following this and as a direct result of the efforts of large corporations, came the establishment of joint committees, entrusted with the powers of a sanitary authority, for the administration of acts for the prevention of rivers pollution, whilst the work of these Committees or Rivers Boards has been extensive and in some cases drastic, the evil seems to have been too deeply rooted at the commencement, and at the present day, in spite of magnificent work, the condition of English rivers passing through large manufacturing districts is extremely bad. No doubt the chaotic state of the laws on the subject has much to do with the slow improvement to be noticed. It can be quite understood that pressure upon manufacturers is followed by complaints on their part of harsh treatment, for their works in the majority of cases have been developed to such an extent that want of space for purification works is only too evident. Various other claims are put forward on their behalf, the strongest of which is possibly that they, being large rate payers, are entitled to have their effluents admitted to the public sewers. Here is shown the ridiculousness of the existing law in that local authorities are bound to give access to the sewers, unless the sewers are only sufficient in size to meet the existing requirements of the community, or unless the admission of the refuse would interfere with the sewers or the treatment of the sewage. The proviso nullifies the act and thus renders its unworkable, for authorities have only to show that their works are

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just sufficient for local conditions and their responsibility ceases. Many local authorities, however, are prepared to admit manufacturing refuse to the sewers, provided that regulations drawn up by themselves are complied with. It must, I think, be admitted that manufacturers are entitled to some little consideration in this matter, for after all, upon them falls a considerable share of the burden of taxation, and some few sanitary authorities have already recognized this by obtaining special acts of Parliament. Foreshadowed legislation will probably at an early date make provision for the universal admission of trade effluents to the sewers, on one of two lines, either preliminary treatment, or payment of fees according to the nature of the effluent and the increased cost of treatment at the sewage works of the authority. This willingness on the part of large authorities to admit trade effluents to the sewers has been found to be very helpful to tanners in the larger sanitary districts. Repeated pressure on the part of Rivers Boards was causing undoubted unpleasantness and uneasiness. Many tanners had not the land for such development as was necessary for their business, and even where this difficulty could be surmounted, the provision of the necessary capital—exceptionally large owing to the strong character of the effluent—tended to cripple an industry which is very fluctuating. Now the way seems clear for brighter understanding It will be seen that on this subject tanneries may be divided into two classes, those having access to the sewers and those which must treat their effluent to render it fit to discharge to a stream.

Before considering any special treatment it may be well to consider the general chemical aspect of river pollution. The power of a river to keep itself pure may be directly related to its power of dissolving oxygen. Thus a river receiving but a small amount of polluting effluent may easily oxidize such polluting matter and recover its original vitality in the course of its flow, especially if in that course are to be found bridges and weirs, passage through and over which considerably helps aeration. Thus a well known English holiday resort actually pumps its drinking water from the river into which, but a few minutes previously, has been discharged the effluent from the sewage works. Thanks to efficient aeration no ill effects have been noted. On the other hand sluggish rivers receiving many effluents never

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recover themselves and thus are said to be polluted. It will be seen that pollution is one of degree, peculiar to local conditions, and consequent upon this that no standardization of effluents is rational or desirable. This is a consideration which it is essential to remember, and which causes great dissatisfaction between contending authorities and mill owners. The main object of treatment of crude effluents may thus be said to be the removal of those constituents which have an adverse influence upon the stream receiving them, in that they prevent the stream recovering its partial or absolute purity. It may at once be said that the most important impurities which it is necessary to remove are the solid matters carried in suspension. Brief consideration of their nature will at once convince one of the necessity for this step. The deposition on the bed and banks of a river of large amounts of solids, each particle of which is covered with organic matter in a high state of putrefaction, must have an undesirable effect. Gradually one sees the formation of grey vegetable growths which are soon covered over with slimy masses and the river then assumes that unpleasant state from which it is so difficult to change it. Having prevented pollution from these bodies, it is still necessary to attack dissolved solids which may by their presence prevent the self restoration of the river to its natural state.

It may be advisable to consider the tests for the putrescibility of an effluent. At the present time no method is known by which this is directly determinable, consequently the number of indirect tests is very great. Possibly the most valuable is the determination of the oxygen absorbing power of the effluent. In contact with an acid solution of potassium permanganate effluents will absorb varying amounts of oxygen in proportion to the organic matter present. If, then, we can reduce this absorption to its reasonably lowest limits, we can assume a great degree of purification. It is quite impossible to tell from this determination alone whether an effluent is putrescible or not, for it is quite conceivable that of two effluents, one may have a larger oxygen absorption than the other, and still be not so disastrous in its effect. Still, this determination is possibly the most helpful that we have. Another test which is relied upon—possibly to too great an extent—is the determination of albuminoid nitrogen. This was

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devised by Wanklyn in 1867 and depends upon the fact that organic nitrogenous bodies are partially oxidized when distilled with alkaline permanganate, liberation of ammonia resulting. This determined, gives an indication of the liability of the sample to undergo putrefactive decomposition. It will be seen that, if treatment results in a diminution of this figure, we may assume purification roughly proportional to the diminution. Of many other methods possibly one of the most helpful is that devised by Scudder, in which the effluent is mixed with tap water fully saturated with oxygen. The diminution of this dissolved oxygen is determined after certain periods and from the rate at which this proceeds one judges the possibility of putrefaction. Of course, these and other methods are really relative, for no strictly quantitative deductions can be drawn from the results.

We have thus far briefly discussed the general aspect of the problems of pollution and its prevention and it is necessary to specially consider its bearing upon our industry. It must be admitted that the treatment of tannery effluents has not progressed to the extent which one might reasonably expect, and in the main this is due to the chaotic state of laws previously described. It is only natural that manufacturers have delayed consideration of the question until the last moment in order that they may take advantage of legislation long overdue. For this reason, apart from description of preliminary treatment in cases where access to large sewage works has been obtained, it will only be possible to suggest lines of full treatment based on achievements in some few cases of exceptional difficulty, or in experimental plant.

Of the waste liquors in a tannery, the soaks, spent liquors and old limes are the really objectionable ones. The other liquors, various wash waters and waste dye liquors from the currying shops and chrome yards, are much more easy of treatment and happily do not influence the treatment to the same extent as those first mentioned. The volume of these liquors run to waste in any tannery is of course a quantity peculiar to that tannery. A tannery having a capacity of 1,500 market hides per week will probably run to waste 25,000 gallons of old tan liquors and 10,000 gallons of old limes; puers and wash waters will account for 75,000 gallons, whilst soaks add 40,000 gallons, making a total of about 150,000 gallons. Of course, these amounts vary

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week by week and must only be regarded as approximate. It is still more difficult to estimate the volume of liquors run from a currying shop, but their effect on the total effluent is in no wise proportional to their volume, as they contain matters which are but moderately polluting.

It is well known that lime liquors and tan liquors are mutually precipitable, and for this reason it is advisable and necessary to have separate drainage for lime liquors. Much bother is experienced where the one drain conveys both liquors to the purification plant, for the precipitation which is so helpful in treatment is obtained before the bulk of the liquors are mixed. In tanneries known to the writer sludging of the drains occurs and, if these be not often cleaned out, back washes occur in running off old limes and one actually gets lime-tannin precipitation and staining in lime pits. The results can readily be imagined.

It is generally necessary to pump the liquors from the drains to precipitation tanks. Here one sees the advisability of separate drainage, for the tanner is greatly helped by the coprecipitation of the various liquors. What generally happens is, that with this lime tannin precipitate a great part of suspended animal matter, fibers, hair, dung, etc., is enclosed and carried down. Here then comes the chemist's first concern and that is the regulation and equalization of these liquors in order that the maximum precipitation may be obtained. To this end it is necessary to decide whether quiescent settlement or continuous flow settlement shall be adopted. In the former method a series of tanks is filled in rotation and each tank is allowed to stand full for a certain time before the top layer is discharged. Two tanks might be sufficient, each having a capacity equal to half a day's flow of waste liquor. In the latter method the waste liquor is allowed to flow continuously through one or several tanks arranged in series. Naturally with this method, in order to ensure slow flow of the liquor, one has to provide tanks of as large a capacity as convenient. If quiescent settlement be adopted the design of the tanks does not call for much skill. Large square wooden tanks, conveniently placed above the ground are necessary. They are fitted, at a suitable height, with a pipe and tap through which the supernatant liquor can be run off to the gutter leading to sewer or filter. In the bottom of the tank is filled a similar pipe and

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tap. Through this the sludge is run off at intervals. On the top of the tanks is placed a gutter, fitted with valves, so that any or all of the tanks may be filled with the waste liquor pumped from the works drains. In practice one then fills each tank in turn. As each tank is filled one gets good mixing of the various liquors and the resultant coprecipitation takes place. It may be, by reason of continued excess of one liquor, that full precipitation is not always attained, and in this case, the addition of precipitants is necessary. By far the best precipitant in our case is sulphate of aluminium. One generally finds that the waste liquors, owing to excess of lime, are alkaline, and this then causes precipitation of aluminium hydrate. This precipitation generally occurs on and around particles of organic matter and causes their deposition. In other extreme cases it may be necessary to use lime as precipitant in conjunction with the aluminium sulphate. Other precipitants on the market in England contain iron salts. This prohibits their use in the treatment of tannery effluents—owing to the dark coloration formed with tannins. These are matters for laboratory investigation. It will be found, however, after a few days control, that the amount of precipitant required for each tank will be a fairly constant quantity, and close chemical control will not always be necessary. After precipitation, settlement is allowed to take place, and at the end of a few hours, this having been effected the top liquor may be run off by the tap provided. It is not necessary to run off the sludge after each settlement for it is generally recognized that remaining sludge helps further precipitation after subsequent filling of the tank. Considerations of space may not allow provision for quiescent settlement, and continuous flow settlement may then be adopted. In this case three or four tanks of as large a capacity as possible are provided. The total capacity obviously depends upon the volume of liquor to be treated, but the tanks should be capable of holding at least half a day's flow of liquor. They are fitted with taps similar to those already described when dealing with tanks for quiescent settlement. With this method the internal arrangement of the tanks calls for consideration. To ensure efficient sludge settlement, boards are fixed so that the liquor flows alternately downwards and upwards from one end of the tank to the other. Especially is this necessary

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when hot dye liquors are intermittently pumped into the tanks, for otherwise these hot liquors would float across the top of the full tank and run away without mixing or treatment. Each tank, similarly constructed, is joined to the next one, and the liquor, with a slight head, thus flows from the inlet of the first to the outlet of the last one. Across the top of the tanks is placed a feed gutter fitted with valves so that any tank may be made the first of the series. The precipitation difficulties are greater when this continuous flow system is adopted, because it is not easy to effectively equalize and mix the various liquors. By laboratory investigation the most suitable amounts of precipitant to add per gallon of waste liquor will be determined. This addition, in the majority of plants, is carried out by running the liquor over a water wheel on the periphery of which are small buckets which pass through milk of lime on the one side and a solution of the aluminium sulphate on the other, and with each revolution deliver definite amounts of these precipitants into the liquor. In practice the liquor is pumped from the works drains over the wheel into the end tank, and having run its course through the tanks it is led away through the gutter to the series or to filters. Precipitation commences in the first tank, and if efficient design has been attained is almost complete when the liquor passes out of the second tank. The accumulation of sludge at the bottom of the baffle boards somewhat helps to retain the finer particles present in the flowing liquor, but by this process larger quantities of sludge are produced than by quiescent settlement. The sludge accumulated will have to be run off at intervals and needs careful attention. Each of these systems has its advantages and drawbacks. Quiescent settlement will need greater attention and therefore the labor cost will be greater than if continuous settlement be adopted. On the other hand, more exact and efficient treatment will be obtained by quiescent settlement; this means a saving in the cost of precipitants. Another point to consider is that quiescent settlement will give the smaller yield of sludge; this is a most important cost saving when one considers the difficulty of disposal. The amount of suspended solids to be removed by settlement varies with the flow of one or other waste liquor.

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An average sample of untreated effluent from a tannery at Burnley gave on different days the following figures:—

	Parts per 100,000.		
	Total	Organic and volatile	Ash
Sample A, solids in suspension	324.0	308.0	16.0
" " " " solution.....	256.0	206.0	50.0
" B, solids in suspension.....	80.0	43.2	36.8
" " " " solution	84.0	26.8	57.2

Naylor gives the following figures in his book "Trades Waste."

	Parts per 100,000.		
	Total	Organic and volatile	Ash
Solids in suspension sample C.....	125.0	11.0	114.0
" " " " D.....	128.0	100.0	28.0
" " " " E.....	106.0	87.0	19.0
" " " " F	82.0	53.0	29.0
Solids in solution sample C.....	298.0	127.0	171.0
" " " " D.....	506.0	168.0	338.0
" " " " E.....	166.0	98.0	68.0
" " " " F	279.0	171.0	108.0

These figures prove what already has been written,—that each effluent demands treatment peculiar to itself, and that no generalization can be made.

We may now be said to have reached the first point of purification mentioned in the general discussion above. The greater part of the suspended solids have been removed, and with them much of the matter in solution which may be polluting, or which may prevent subsequent purification. One must not lose sight of the fact that the more complete the removal of soluble tannins at this stage the easier the attainment of success in treatment, for the well known oxygen absorbing power of alkaline tannates has a serious effect in after stages. This too is the stage where responsibility ceases for those tanners who are fortunate in having access to the public sewers, the effluent in this case generally being run off through sieves to the drain. This final sieving is a requirement of most public authorities.

The sludge has still to be dealt with but consideration of its treatment may be postponed.

From this point treatment of the effluent becomes difficult, and it will be the duty of the writer to point out the trend of modern developments, and to suggest what, to him seem the most hope-

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ful lines of investigation. Up to the present day the tanner has possibly considered his obligations to be fully met by running his effluent over coke and ashes and thence to the stream. This latter treatment as generally carried out has little purifying action. More efficient purification may, however, be attained by constructing and operating filters in a manner which has proved so effective in the case of sewage purification works.

Early English investigation in the treatment of sewage showed the necessity for purification beyond the stage of precipitation, and to Frankland must be given the credit of pioneer work. The Royal Commission of 1868 in its third report issued in 1876 adopted the view that land treatment was the best and most natural method of sewage purification. Frankland, as a member of this Commission, recognized the difficulties attendant upon the acquirement of sufficient land for this treatment, and instigated experiments with a view to increasing the amount of sewage which could be treated upon a definite area of land. He found that choking of land did not occur if the sewage was applied in small doses. His method was to dose the land with the sewage at definite intervals, carefully regulating the volume applied to limits which he found to be most suitable for the particular soil in use. Thus, for a town of 10,000 inhabitants be considered that five acres of land filters should suffice if the land were divided into four equal plots and the sewage applied to one plot after the other, each for six hours. These conclusions were the result of his laboratory experiments, in which, by the use of glass cylinders filled with soil through which was inserted a glass tube to ensure aeration, he obtained effluents, non-putrescible and containing nitrates. His methods may well be regarded as the basis of modern biological methods of sewage treatment, but the credit for practical extension of the principles laid down by him must be given to the Massachusetts State Board of Health. Experiments were carried out by the Board's officers with many filters composel of various materials. Their method was to fill tanks with the material under investigation, and the filter thus formed was then treated with sewage at definite intervals, periods of rest being allowed between successive applications. Some gravel filters provided with artificial aeration received screened sewage at the

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rate of 350,000 gallons per acre per day and gave purification of 80 per cent. as measured by the diminution of the oxygen absorbed. Experiments in England led to the development of contact beds in which the sewage stood for some hours, and after the sewage was run off, the bed rested for a similar interval to recover its powers of purification. Corbett in Salford recognized the principle, laid down by Frankland and the Massachusetts Board, that the liquid should always be allowed to freely flow away. To ensure even distribution and aeration he discharged the sewage on to beds of coarse material by means of spray jets from which the sewage was forced by pressure. To further attain efficiency he adopted open ventilated flows under the filter. One great difficulty at this time was the proper distribution of the sewage over the material forming the filter. It was found that with the use of coarse material, the sewage simply passed through the bed unpurified. Massachusetts experimenters tried to overcome this by the use of syphons which discharged the sewage on to the filter at regular intervals. Corbett's spray jets were devised to attain the same end, but later experiments have shown that by the use of graded materials, a fine layer at the top and coarser ones toward the bottom, this difficulty is overcome.

It would be beyond the scope of this article to fully discuss the theories of the actions which go on in this method of sewage purification. Frankland assumed that the dissolved organic matters were oxidized by the air contained in the pores of the soil whilst the sewage was percolating through the soil. Work by different investigators on nitrification in soil by micro-organisms led the Massachusetts experimenters to explain the purification by the assumption that bacteria in the sewage and in the filter effected mineralization during actual flow of the sewage through the filter. Dunbar attacks this and other theories, and at the same time puts forward the theory of absorption. He assumes that dissolved organic matters are first separated from the sewage during its passage through the filter, and are retained in the filter, to be decomposed and oxidized by micro-organisms during succeeding periods of rest. He shows that dissolved organic matters pass through the finest filtering materials without diminution in quantity, and he therefore dismisses the possibility of

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mechanical filtration. Similarly he dismisses the general possibility of chemical combination between the organic matters in solution and the filter material, and finally, he advances his absorption theory. In support, he shows that whilst a filter receiving sewage greater in volume than its water retaining capacity delivers an effluent containing slightly less organic matter than the original sewage, yet if the volume applied be less than the water retaining capacity, the putrescible matters are to a small extent removed. Repeated dosing shows increased retention of putrescible matters until purification to the extent of 60 per cent. is attained. Thus organic matter is quickly retained although it was present in solution. He theorizes that the particles of sand and other matters forming the filter gradually become coated with a film of gelatinous substance of increasing thickness. This gelatinous coating, on examination, is found to contain bacteria and low forms of life as well as amorphous substances varying with the nature of the sewage and filter. This film becomes thicker and thicker; diminishing the volume of the pores but increasing the water retaining capacity of the filter. When the effluent contains nitrates the filter is assumed to be mature, the last stage of mineralization and oxidation having been reached. It is assumed that the film has a honey comb structure, and having an internal as well as an external surface can absorb gases and also many organic substances of high molecular weight. Assuming absorption as explained by Dunbar, it is easy to see that the more thorough the contact between the sewage and the material forming the filter, the more thorough the purification. Corbett's sprays then seem to help matters to a considerable extent, for as the sewage falls in single drops, each drop spreads over the surface of the material and gradually drops from one piece to another, everything tending to help absorption of the dissolved organic matter. This also shows the weak points of contact beds into which the sewage is quickly delivered. The extensive film on the material being washed off owing to strength of current, efficient contact cannot take place nor can aeration be effected to the required extent. It must be remembered that it is this contact and aeration which is so necessary in order to ensure activity of bacteria and the attendant oxidation. Percolating filters need not be constructed of fine

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material if efficient distribution be attained, and consequently they are less costly in upkeep. Contact beds tend to clog up, but with a carefully graded percolating filter having fine material at the top little trouble is experienced.

The development of bacterial treatment of sewage having been briefly sketched, the real question now before us is the application of such methods to the treatment of partially purified waste liquors. Theoretically it would seem, that providing the filter be properly matured with the most suitable organism, it should be possible to purify any special trade waste, that is, in the absence of matters which will inhibit bacterial action. Dunbar has proved that, with sewage, inhibition does occur if antiseptics be present in the sewage, the action of the filter gradually diminishing until no purification takes place. So far as we are concerned with tannery effluents, practically the only antiseptic which, may have this action is sulphide of arsenic. Experiments about to be described will show that this has been successfully combated.

In England, little bacterial purification of tannery effluents has been attempted, and in the few instances where success has been attained, no results have been published. One has therefore to look to the United States for pioneer work which is undoubtedly important. The Massachusetts Board of Health has, in its report for 1909, some interesting results which must be of interest to all concerned in the problem. The Board's special powers of investigation on the large scale are noteworthy and clearly show the need for development in a similar direction in the case of the English Rivers Boards. The Royal Commission on sewage disposal, appointed in 1898, has recommended the formation of a Central Authority endowed with such powers of investigation, and to the writer it has always appeared that help of this character must, in the end, lead to the quicker and more efficient cleansing of our streams.

Of the experiments described in the report of H. W. Clark, chemist to the Massachusetts Board, the following are possibly the most interesting:

Tannery A.—This tannery was engaged in tanning and currying sheep skins. It discharged an effluent varying in daily volume between 20,000 to 50,000 gallons. This effluent was offen-

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sive in character and highly colored, but did not contain matters which would prevent bacterial action. Nitrification was therefore easily effected. The first attempts to treat this effluent on a sand filter, two feet in depth, were not very satisfactory. Although the effluent, applied at the rate of 25,000 gallons per acre per day, had its oxygen absorbed figure reduced from 61.25 to 7.92 parts per 100,000, the filter soon became clogged, owing to suspended matter in the effluent. In face of this difficulty precipitation and sedimentation was tried. It was found that mixture with the old limes, followed by settlement, effected removal of 60 per cent. of the organic matter in solution. The settled liquor was still very impure, and was then applied, at the rate of 30,000 gallons per acre per day, to a filter containing fine sand to the depth of four feet. It being winter when the experiment was started there was little nitrification at first, but this increased as the weather became warmer, and for two and a half years an effluent was obtained which was clear and colorless, contained large amounts of nitrates, and had a low oxygen absorbed figure. It is interesting to note the analyses of the precipitated liquors run onto the filter, and of the effluent from the filter. We find considerable diminution in the ammonia content, whilst the nitrates present increase from 0.17 to 9.96 parts per 100,000. At the same time the albuminoid nitrogen diminishes from 2.39 to 0.23 parts, and the oxygen absorbed diminishes from 46.66 to 1.79 parts per 100,000. Further experiments at this tannery were with a coke strainer containing 2 feet in depth of coke, the upper portion being coke breeze and the lower portion coarser coke. This strainer was operated at the rate of 250,000 gallons per acre per day, and was successful in removing about 80 per cent. of the organic matters present, still giving an effluent which was polluting and which required to be treated on a sand filter. The purification effected by this coke strainer may be noted from the following results. The albuminoid nitrogen was diminished from 4.45 to 0.35 parts per 100,000, and the oxygen absorbed diminished from 95.20 to 3.96 parts per 100,000. Nitrates were produced to the extent of 0.56 parts per 100,000.

Tannery B.—This tannery was treating cured skins and for this reason naphthalene was found in the waste liquors. Arsenic limes were used in depilation and consequently arsenic was

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found in the waste liquors to a considerable extent. Precipitation by means of the old limes was first effected, settlement followed, and then the liquor was treated on filters. No. 1 a sand filter, 4.5 feet in depth, produced a good effluent, but the extent of nitrification was considerably affected by variations in the amount of arsenic present in the liquors—the amounts being so high that, in general, bacterial growth was checked. The presence of arsenic, as above stated, caused some trouble, and it was necessary to find some means of removal. Precipitation by means of the waste limes caused precipitation of a considerable proportion of the arsenic. It was found that whilst the liquors delivered to the precipitation tanks contained an average amount of 8.54 parts As_2O_3 per 100,000, the liquors fed onto filters only contained an average of 1.67 parts As_2O_3 per 100,000. Although this purification is considerable, it is insufficient when we consider that bacterial purification is to follow. The Board's chemist found that by passing through a strainer of coke breeze almost entire elimination of arsenic occurred, an average of 0.08 parts As_2O_3 per 100,000 being found. He attributes this to the presence of iron in the coke. It is interesting to note that examination of the coke bed showed that the greater part of the arsenic was retained on the upper few inches of the strainer. Evidently as the result of these investigations, a coke filter was constructed containing 2 feet in depth of coke breeze. The settled liquors were applied to this filter at the rate of 100,000 gallons per acre per day, and the effluent from this was then applied at the same rate to a sand filter 4.5 feet in depth. Whilst the settled liquor contained matters giving 4.70 parts of albuminoid nitrogen per 100,000, the coke bed reduced this to 0.77 parts, and the sand filter further reduced the figure to 0.11 parts. Similarly the oxygen absorbed figure was reduced from 40.50 to 10.57 parts per 100,000 by the coke bed treatment, and to 3.52 parts by the sand filter. Nitrates were produced in considerable amounts, the coke bed effluent giving 0.12 parts per 100,000; this figure was increased by the sand filter to 1.97 parts. This plant worked well for some considerable time, producing an effluent which was uniformly good.

Other experiments of a similar nature were carried out at other tanneries but sufficient has been quoted in this article to demon-

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strate the extreme importance of the work of the Board's Chemist. He has conclusively shown that it is possible to well purify tannery effluents by means of precipitation, straining through coke breeze, or in extreme cases through coke and iron filings, and then by final filtrations through sand or similar filters.

In the Journal of the Society of Chemical Industry for February 28, 1911, Dr. Fowler of Manchester publishes some interesting experiments on the treatment of effluents from ammonia recovery plants. Great difficulty has hitherto been experienced in the treatment of this class of effluent, the presence of phenol and thiocyanates being most injurious to fish life. At the same time these bodies tend to prevent self recovery of the stream. Fowler has shown that solutions of phenol and thiocyanate can be purified by means of bacterial filters; in the case of phenol by the action of a single species of organism, and in the case of thiocyanate, by the combined action of several organisms. What is more important is that he finds this oxidation to go on without denitrification, and therefore we still have the possibility of further purification after entry to streams. Employing works effluents, he finds, that by distribution over a filter 5 feet deep, composed of clinker, carefully graded from ¼ in. to 6 inches, he can obtain a purification of 98 per cent. as measured by the oxygen absorbed figure. This, of course, does not directly concern us as leather trades chemists, but it shows the possibilities of the method which is slowly being extended in application. Similarly, in the laboratory of the West Riding of Yorkshire Rivers Board, it has been found possible to purify, by bacterial filters, effluents from wool scouring mills. These effluents had previously caused excessive trouble, precipitation methods alone being found to be almost totally inadequate in practice.

With the foregoing results before us, it should not be difficult to devise a scheme for the successful treatment of tanning effluents. It is, however, quite beyond the powers of the writer to give detailed specifications. Each works will vary in its effluent so as to render this impossible.

In the first place, discrimination should be shown in the collection of the various waste liquors. It should be the object of the chemist to prevent precipitation in gulleys and drains, for besides saving considerable labor cost in cleaning, one helps pre-

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cipitation in the settling tanks. Another disadvantage of faulty design is back washing into limes caused by excessive sludging in drains. All this causes considerable expense and inconvenience, and should be carefully attended to. If waste liquors are, as far as convenient, grouped together before entry into the precipitation tanks much may be saved in the cost of precipitants.

The design of settling and precipitation tanks is important, and should be carried out to serve efficient and quick mixing. This having been effected, it is then essential that the capacity be sufficiently large to ensure good settlement. This can be done by either of two methods, provision of tanks each to hold at least half a day's flow, or provision of tanks of sufficient capacity to ensure slow rates of flow.

Having effected precipitation, the bacterial treatment to follow should be carried out on the general lines sketched above. To the writer's mind, possibly the best lines upon which to work would be the provision of two filters, both composed of carefully graduated coke breeze to the depth of 5 or 6 feet. As an alternative, the first might be constructed of coke breeze and the second of similarly graduated clinker. The need for continuous control might be less than if a sand filter were used, and from work published by Dunbar it would seem that coke or clinker filters would have longer life, frequent cleansing being obviated. One important feature is the maturing of the filter, and in the United Kingdom the most efficient method is inoculation from a sewage filter. Where this is inconvenient, treatment with cow dung will answer quite as well. Maturing will undoubtedly be more speedy if the works be commenced in the summer months, but when once matured, filters will, if properly controlled, work well through all weathers.

One of the most important considerations, in the light of the above summary of progress in treatment, is the method of distribution to be adopted. Present day sewage engineers generally favor rotating distributors as being the most efficient in practice. With a little skill, however, it should be quite possible to well distribute the settled liquor by means of troughs laid on the top of the filter. This will effect saving in initial charges and in cost of upkeep.

The standard of effluent to be obtained cannot be definitely pre-

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scribed. It must obviously depend upon the nature of the stream into which it is to be discharged. One might, however, suggest the following limits as being desirable, and generally speaking, quite fair.

	Parts per 100,000
Oxygen absorbed in 4 hours at 80° F	below 2.0
Solids in suspension	below 10.0

One cannot suggest standards for the albuminoid nitrogen or for the nitrate figures. Reduction of the former generally ensures increased nitrification and lessened oxygen absorption. Both must therefore be considered in conjunction with the oxygen absorbed figure.

One matter referred to above is the question of sludge disposal. The sludge obtained from settling tanks has undoubtedly a good manurial value and is consequently of value to farmers. As run off from the tanks its water content may generally be as high as 80 per cent., and the difficulty of transport in this state, coupled with its excessive cost, renders drying necessary. No tannery in England produces sufficient sludge to warrant laying down of sludge pressing plant, and tanners have had to adopt other means of treatment. Manure merchants are generally willing and anxious to undertake the removal of the sludge. They recognize its value, especially in combination with other waste products. Their method of treatment is to run off the sludge onto heaps of stable manure. Intimate mixing is then carried out by repeated forking and turning over. In this way a really good saleable manure is obtained which can easily be disposed of. This is an arrangement generally carried out by the majority of tanners and seems to be satisfactory to all concerned. In American tanneries where much larger quantities of sludge must be dealt with it may be profitable to install sludge presses. The cake then obtained will undoubtedly have a good manurial value and should be easy of disposal. Such presses are in general use in sewage works and need no description in this article.

In a subsequent paper the writer hopes to give a resumé of standard methods of analysis as carried out in the laboratory of the West Riding of Yorkshire Rivers Board. This may, he hopes, be helpful in the attainment of that efficient control which is so necessary and desirable.

Leeds, England.

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DIFFUSION OF THE TANNINS THROUGH GELATIN JELLY.

By A. W. Hoppenstedt.

Very little research work seems to have been undertaken in order to determine the relative penetration of the different tannins through hide, which in our present-day combination tannages, would appear of equal importance to the study of weight-giving, acid-making and other properties. The most important work published thus far, which gives some enlightenment on this subject, is the one of Youl and Griffith, (Journal Society of Chemical Industry, 1901, 426.) though the deductions made by the authors regarding the penetration of the tannins, by assuming that by means of the determination of the hide-substance in the leather during regular stages in the tanning, the amount of penetration was indicated, hardly seem justifiable, for the molecular and combining weights of the tannins would have to be taken into consideration. C. Koerner (Collegium, 1903, 2, 100-102.) has determined the molecular weights of a number of the tannins and states that quebracho tannin is 1272, mimosa tannin 1063, chestnut-wood tannin 1139 and oak-wood tannin 1148. These values show the difference in the tannins.

In order to satisfactorily compare the diffusibility of the different tannins, a gel was required in which the progress of the diffusion could be readily observed and studied, and which would allow of strictly uniform conditions and be analogous to hide-substance. Gelatin jelly naturally suggested itself as the most promising medium and after several preliminary tests proved satisfactory.

Experiments were then conducted as follows: A 5 per cent. solution of pure neutral gelatin was made up and poured into large test-tubes, filling the same about one-third full. Care was exercised to have the strata of the gel identical in each tube. Another 5 per cent. solution of the gelatin was made up containing 0.015 per cent. of ferric ammonium alum and placed in another set of test tubes in the same manner and corresponding to the first. The gelatin was then allowed to set to a jelly. The object of having two sets of tubes, one with gelatin only and the other with gelatin containing a very small quantity of

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a ferric salt, was to observe the diffusion of the color in one case and in the other, to have the diffusing materials produce a black, whereby the diffusion could be more readily observed and include all matters giving a reaction with iron, which, if colorless, would otherwise escape notice. It may be of interest to note here that the non-tannins of all tanning materials give a reaction with iron. Solutions of the following tanning materials, containing 4 gms. of tannin per liter, were then made up.

1. Clarified Quebracho Extract (Bisulphited)
2. Ordinary Quebracho Extract
3. Chestnut Extract
4. Hemlock Extract
5. Oak Extract
6. Gambier
7. Myrobalans
8. Valonia
9. Divi-Divi
10. Algarobilla
11. Mangrove Bark (African)
12. Mangrove Bark (Venezuelan)
13. Sumac (Virginia)
14. Sumac (Sicily)
15. Hemlock Bark (Pennsylvania)
16. Hemlock Bark (Wisconsin)

These solutions were poured into the tubes on top of the gelatin jelly, the height of the liquor being made identical in each one and equivalent to the gelatin jelly below. Thus the conditions in the tubes were identical in every way, and considering the great difference in the specific gravity of the gelatin jelly and the tan solutions, it is evident that any diffusion could not be due to gravitation.

The diffusion begins at once and becomes plainly visible with the rapidly diffusing materials after a very short time. It progresses steadily and the different materials maintain their relative positions throughout. Photographs were taken of the tests after 3 days contact and these are shown in Figs. 1 to 4. Fig. 1 shows the tubes with the pure gelatin jelly on the bottom and the tannin solutions on the top, and Fig. 2 the same tubes

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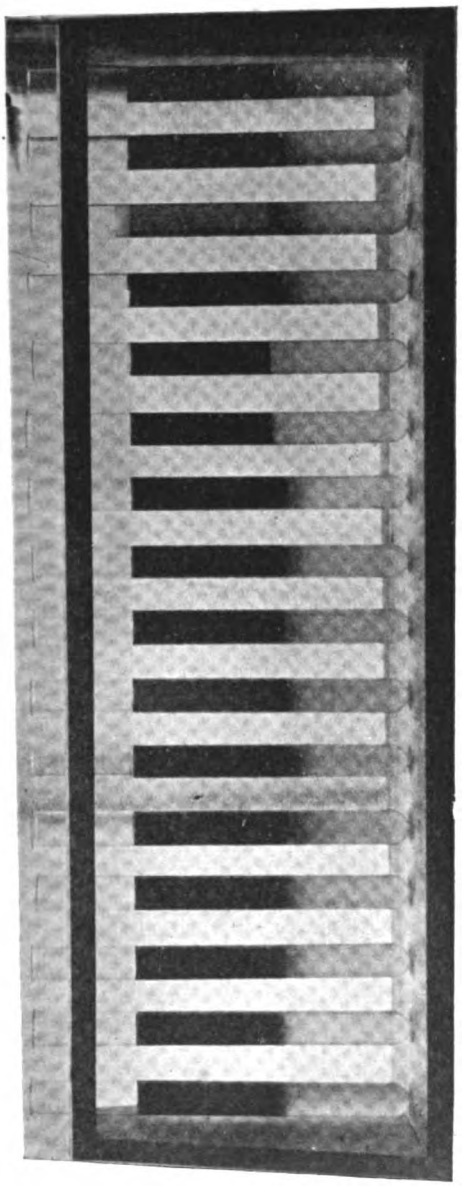

Fig. 1.—Pure gelatin. After three days' contact.

1. Quebracho ext. (clar.)
2. Quebracho ext. (ord.)
3. Chestnut extract.
4. Hemlock extract.
5. Oak extract.
6. Gambier.
7. Myrobalans.
8. Valonia.
9. Divi-Divi.
10. Algarobilla.
11. Mangrove (Afr.).
12. Mangrove (Ven.).
13. Sumac (Va.).
14. Sumac (Sic.).
15. Hemlock (Penn.).
16. Hemlock (Wis.).

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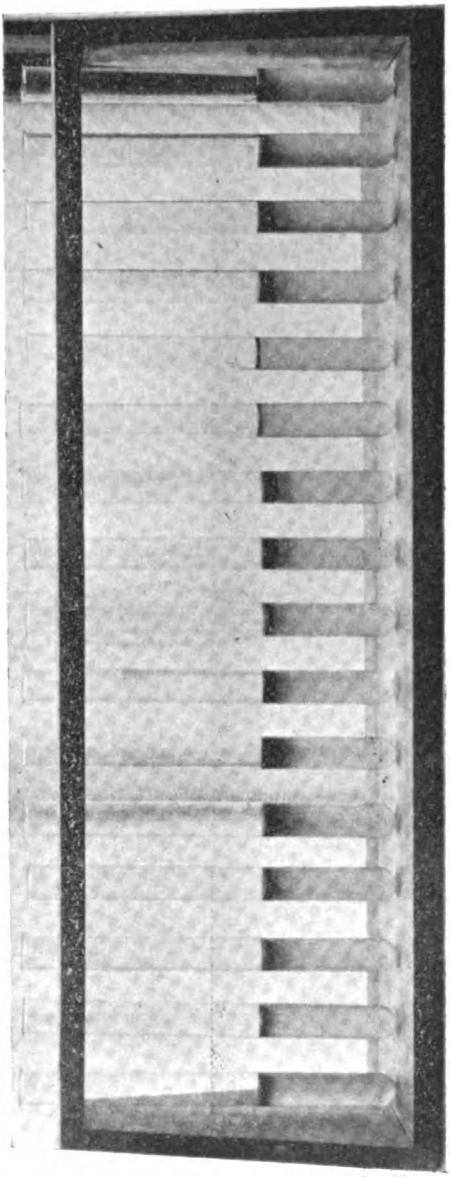

Fig. 2.—Pure gelatin. After three days' contact. Tannin solutions poured out.

1. Quebracho ext. (clar.)
2. Quebracho ext. (ord.)
3. Chestnut extract.
4. Hemlock extract.
5. Oak extract.
6. Gambier.
7. Myrobalans.
8. Valonia.
9. Divi Divi.
10. Algarobilla.
11. Mangrove (Afr.).
12. Mangrove (Ven.).
13. Sumac (Va.).
14. Sumac (Sic.).
15. Hemlock (Penn.).
16. Hemlock (Wis.).

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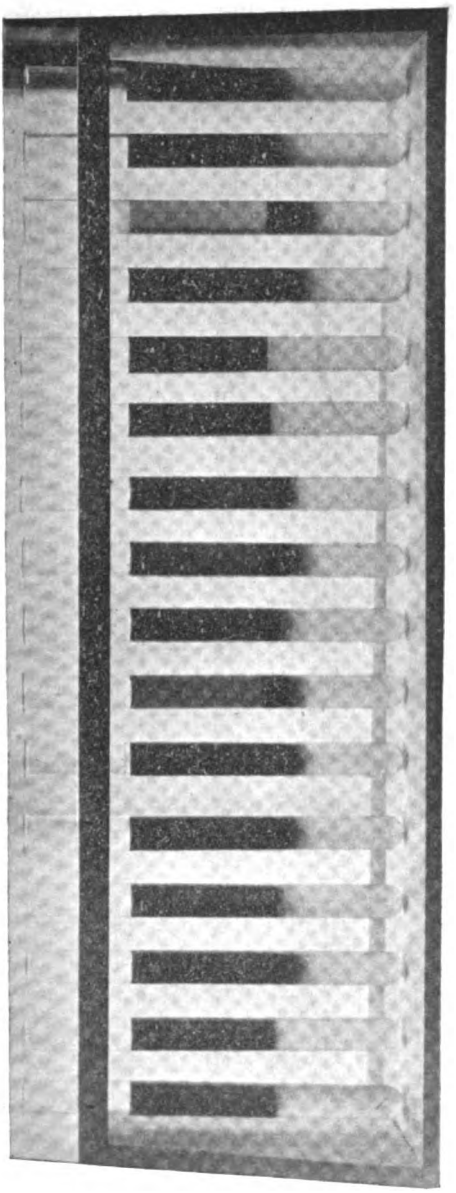

Fig. 3.—Gelatin and iron. After three days' contact.

1. Quebracho ext. (clar.)
2. Quebracho ext. (ord.).
3. Chestnut extract.
4. Hemlock extract.
5. Oak extract.
6. Gambier.
7. Myrobalans.
8. Valonia,
9. Divi-Divi.
10. Algarobilla.
11. Mangrove (Afr.).
12. Mangrove (Ven.).
13. Sumac (Va.).
14. Sumac (Sic.).
15. Hemlock (Penn.).
16. Hemlock (Wis.).

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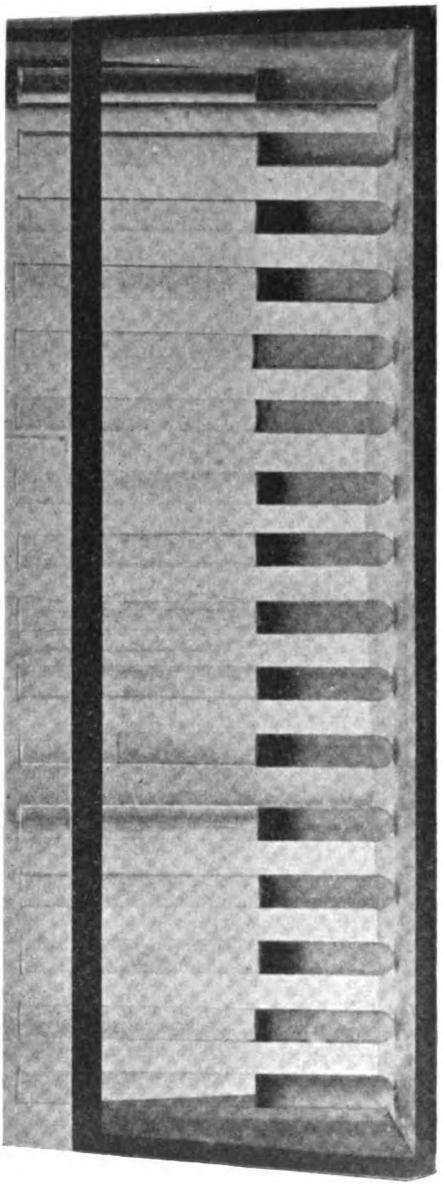

Fig. 4.—Gelatin and iron. After three days' contact. Tannin solutions poured out.

1. Quebracho ext. (clar.)
2. Quebracho ext. (ord.)
3. Chestnut extract.
4. Hemlock extract.
5. Oak extract.
6. Gambier.
7. Myrobalans.
8. Valonia.
9. Divi-Divi.
10. Algarobilla.
11. Mangrove (Afr.).
12. Mangrove (Ven.).
13. Sumac (Va.).
14. Sumac (Sic.).
15. Hemlock (Penn.).
16. Hemlock (Wis.).

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after pouring out the supernatant tannin solutions in order to show more clearly the diffusion into the gelatin. Figs. 3 and 4 show the tubes with the gelatin and iron, otherwise corresponding to Figs. 1 and 2. The materials presented the following order in diffusing power.

1. Sumac (Sicily)
2. Sumac (Virginia)
3. Divi-Divi
4. Gambier
5. Chestnut Extract
6. Myrobalans
7. Oak Extract
8. Valonia
9. Algarobilla
10. Hemlock Bark (Wisconsin)
11. Hemlock Bark (Pennsylvania)
12. Hemlock Extract
13. Ordinary Quebracho Extract
14. Clarified Quebracho Extract
15. Mangrove Bark (African)
16. Mangrove Bark (Venezuelan)

Sicily sumac showed the greatest diffusion, followed closely by Virginia sumac, which in turn was followed closely by divi-divi, gambier, chestnut, myrobalans and oak. Valonia and algarobilla came next, followed by the two hemlock barks and hemlock extract which were very nearly alike. These were then followed by the two quebracho extracts which were also nearly alike and showed a marked lack of diffusing power. The two mangrove bark followed, being practically alike and barely showing any diffusion at all.

These results are not so readily seen from Figs. 1 and 2 as from Figs. 3 and 4 as the light has produced some misleading effects on the photographic plate. In Figs. 3 and 4, the diffusion can be readily compared, the black produced with the iron having

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eliminated these faults. The relationship of the diffusion in the pure gelatin and the gelatin containing iron seemingly was the same. Of the seven main tanning materials, quebracho, hemlock, oak, chestnut, mangrove, valonia and myrobalans, used in the tannage of heavy leathers, chestnut showed the greatest penetration, myrobalans, oak, valonia, hemlock, quebracho and mangrove following in the order named.

The first interesting feature noted in these experiments was that the fluorescent substance of the oak extract has great diffusing power, making itself apparent almost immediately after the solution of the extract had been poured on the gelatin jelly and appearing as a bright fluorescent ring. This fluorescent substance continued to diffuse rapidly and penetrated the greater part of the gelatin in the tube. In Figs. 1 and 2, the oak extract would appear as showing the greatest diffusion of tannin, but this was caused by the above mentioned fluorescence.

The most striking effect to be noted in these experiments is the lack of diffusion of both mangrove barks. These solutions only barely penetrated the gelatin, which behavior may bear some relationship to Eitner's contention (Der Gerber, 1907, 780, 61.) that mangrove is not a true tannin but a substance between a vegetable coloring matter and a tannin.

The behavior of the quebracho extracts is also very remarkable and requires careful consideration. On the supposition that possibly the high tannin and low non-tannins of this material played an important part, tests were carried out with pure tannin (Merck's Highest Purity) in the exact manner as the tests with the tanning materials. The diffusion of the pure tannin was rapid and resembled the results obtained with the oak extract. This would tend to show that the high tannin and low non-tannins were not the influencing factor but presumably the tannin itself. The author regrets that the tests with the pure tannin are not shown on the photographs with the other materials, the reason being that these were carried out after the exposures had been made. It was supposed that the clarified quebracho extract, containing a large amount of sodium sulphate and sulphur compounds, would diffuse more rapidly than the ordinary extract, though the opposite was apparently the case.

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It was hoped that possibly some distinct difference would be noted between the Pennsylvania and Wisconsin hemlock barks, for it has long been the contention of practical tanners that these two apparently identical materials give very different results in the tannery. The diffusing properties were found to be very much alike, Wisconsin hemlock possibly a trifle ahead, and no difference in their action was noted.

It is interesting to note the layers or rings formed by some of the materials, also that some of these were darker than the supernatant tannin solution. The theory advanced by Ostwald (Allg. Chemie II., 778—780.) regarding the formation of layers of supersaturated solution, may also apply here. The same phenomenon was also noted by Procter and Law (Journal Society of Chemical Industry, 1909, 297—299.) with the diffusion of chromium, iron and aluminium salts through gelatin jelly. Another interesting feature observed was that all the blacks produced in the gel, by the catechol as well as the pyrogallol tannins, were blue blacks. The apparent difference in the diffusing power of the pyrogallol and catechol tannins is noticeable. All of the pyrogallol tannins diffused more or less rapidly while only two of the catechol tannins, oak and gambier, did. As oak apparently contains some pyrogallol tannin besides the catechol one, this may explain the behavior of this material and thus leaves gambier the exception.

It is evident from these and other experiments that gelatin jelly well deserves recognition as a valuable medium for readily observing and studying many subjects of interest and value to the leather industry. The experiments cover only a very small part of the field open for investigation and various further studies readily suggest themselves, the most apparent being the influence of different salts and acids in the hide and tan liquors on the penetration of the tannins, the influence exerted by high and low non-tannins, and the deliming action of the different acids, alone, in mixtures, and in the presence of different tanning materials and salts.

Laboratory of Schoellkopf & Co.,
Buffalo, N. Y.

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THE CONSTITUTION OF TANNIC ACID.[1] [2]

By M. Nierenstein.

The use of tannic acid in the dyeing industry dates back to the earliest periods of our civilization, but only in the middle ages (about 1330) do we find it definitely recognized as a black dye (the old German "swarte") when it was used in conjunction with iron salts. It is on record that the uniforms of the soldiers enlisted by Bernhard von Rohrbach (1459) were of three colors—red, white and black—which met in "mitten uff der Hosen." The black thus used was a gall-extract. At one time tannic acid was much used as a black dye and was greatly favored by the Dukes of Austria. This was also the case at the time when Europe was trying to rebuff the invading foreign dyes, such as indigo and other foreign woods. It was then found necessary to encourage the home industries, and recommendations were made by the different guilds promoting galls to the rank of an officially recognized dye (about 1540). The popularity of galls was, however, of short duration. They soon lost importance, especially as they were used in conjunction with vitriol, and for a time dyeing with galls was strongly prohibited, the punishment being at least three months' imprisonment. This prohibition, however, resulted apparently in a greater demand for galls, to judge by the prices, which had gone up from 8 gulden the "Ballen" to 26 gulden in nine years (1598—1607).

The present use of tannic acid as a mordant is so well known to the members of this Society that I had better refrain from speaking about it. I also need not discuss its use in the preparation of ink or in medicine.

Tannic acid, or as it was called for some time the principium adstringens, was isolated from the common oak-gall by Scheele in 1787. In the same year appeared two communications, one by Kunzemüller, the other by Richter, on the same subject.

[1] From the "Journal of the Society of Dyers and Colorists," February, 1911. No. 2, Vol. xxvii, through *Collegium*.

[2] For all references to the literature of the subject see M. Nierenstein, Chemie der Gerbstoffe; M. Nierenstein, Der Gerbstoffe (Biochemisches Handlexikon, Vol. vii.).

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However, it is more or less certain that Richter's product was not tannic acid but pyrogallol, which was thus discovered by him for the first time. The presence of the principium adstringens in the gall was known long before Scheele's time, and we find it mentioned in a list by Pliny of astringent plants. Scheele's work was continued by Dizé (1791), Deyeux (1793), Hausmann (1795), Bartholdi (1799), and Proust (1799). The latter introduced the name "tannin." Tannic acid was also studied by Humphry Davy (1803—1804), to whom the principles of the present hide powder method for the analysis of tannins are due. Davy carried out his estimations by soaking a piece of hide in the solution and weighing it before and after. The difficulties of such a method are obvious, but when one considers the details of our present methods one can regard his results fairly correct and satisfactory. Since the days of Humphry Davy nearly 140 different methods for the estimation of tannins have been described.

Guillot (1801), Trommsdorf (1804), and Bouillon-Lagrange (1805) continued Proust's work and published methods claiming to be improvements on those of Proust's original ones. Ster Turner (1812) even went so far as to insist that he had prepared "pure" tannin. Wüttig (1816) disproved Ster Turner's contention, and came to the conclusion that the principium adstringens, and also the so-called tannin, is an acid, and introduced for this product the name "tannic acid." Ster Turner's and Wüttig's controversy has often been repeated during the investigation of tannic acid. There are now, and perhaps will be for some time to come, workers who believe in the existence of a simple product commonly known as tannic acid. These workers claim to have isolated the pure tannic acid. It is only necessary to refer to the late publications of this year by Iljin and Manning. However, to speak bluntly, I am fully convinced that Ster Turner, as well as these two workers, are in the wrong. History only repeats itself.

Berzelius (1827) proposed for tannic acid $C_{18}H_{18}O_{12}$, which formula was also accepted by Pelouze (1834), who at the same time discovered that tannic acid yields on hydrolysis gallic acid. Liebig (1834) proposed $C_{18}H_{16}O_{12}$ for tannic acid, and pointed

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out that it yields on combustion H_2O and CO_2, and that it contained no nitrogen. The observation that nitrogen is absent in tannic acid was also made by Guillot (1801), Hühnefeld (1836), Mulder (1839), and Gorup-Besanez (1859).

In 1850 Mulder proposed $C_{28}H_{18}O_{17}$ for tannic acid, and laid great stress on the fact that tannic acid formed gallic acid on hydrolysis as previously mentioned. Similar importance was given to this observation by Robiquet (1839) and Larocque (1841).

Strecker (1852—1854) proposed for tannic acid, $C_{40}H_{18}O_{26}$ or $C_{54}H_{44}O_{34}$, thus regarding it as a glucoside of two mols. gallic acid and one mol. of sugar. The view that tannic acid is a glucoside has often been a vexed point in the discussion of tannic acid. This view had and still has its supporters. Robiquet (1854) Rochleder (1856), and Kawalier (1858) denied its glucosidic character, whereas Schiff (1870) and also Froda (1878) regarded it as a glucoside. On the other hand, Wehmer and Tollens (1888), and also Utz (1905), experts on the chemistry of sugar, have come to the conclusion that pure tannic acid does not contain even traces of sugar. A similar view has been expressed by Pottevin (1901). The latter has made a careful study of this question. Lately, Feist (1908) has once more brought forward a glucoside formula for tannic acid. Feist considers tannic acid to be $C_{27}H_{22}O_{17}$ or $C_{27}H_{24}O_{18}$ (the glucoside of two mols. of gallic acid and one mol. of sugar). Nierenstein (1909), on the other hand, has detannized tannic acid with casein, and according to his work, "Tanninum lev. pur. Schering," does not contain even traces of sugar. His work has been repeated by Sisley (1909), who concludes: "Je suis tout absolument d'accord avec Nierenstein pour reconnaître que l'acide gallotannique n'est pas un glucoside." By some others workers, however, Herzig and Renner (1909), and also Manning (1910), who regards tannic acid to be a glucoside of one mol. gallic acid and five mol. sugar, the glucoside formula for tannic acid is still adhered to. I am of the opinion that all these workers have not sufficiently removed both tannic and gallic acids, and their positive results are due to the presence of these acids, which, as it is well known, reduce Fehling's solution.

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We now return to the work done with reference to the constitution of tannic acid. In 1847 Wetherill proposed for tannic acid $C_{14}H_6O_9$. Wetherill's formula has since been accepted by Kawalier (1858), Schiff (1870), who changed it into $C_{14}H_{10}O_9$ (digallic acid), and Löwe (1873), who on the other hand doubled it and regarded it to be $C_{28}H_{24}O_{18}$. The formula $C_{14}H_{10}O_9$ has also been accepted by Dekker (1906), Nierenstein (1907), and others.

Only recently (1909) Iljin has pointed out that tannic acid analyzed by him contained C=54.13 per cent. and H=3.22 per cent. whereas $C_{14}H_{10}O_9$ requires C=52.13 per cent. and H=3.41 per cent. I hence append the following table giving the analytical data found by different workers, and which by no means confirm Iljin's observations:—

Berzelius (1827)	C = 51.5	H = 3.8
Pelouze (1834)	C = 51.5	H = 4.1
Liebig (1834)	C = 52.5	H = 4.1
Wetherill (1847)	C = 50.6	H = 3.6
Mulder (1848)	C = 52.8	H = 3.9
v. Bijlert (1848)	C = 51.8	H = 3.7
Strecker (1852)	C = 52.4	H = 3.5
Schiff (1871)	C = 51.7	H = 3.8
Löwe (1872)	C = 51.8	H = 3.7
Gautier (1880)	C = 51.2	H = 3.3
Gautier (1880)	C = 53.2	H = 3.0
Walden (1890)	C = 52.27—52.85	H = 3.76—7.33
Trimble (1892)	C = 52.1	H = 3.5
De Graffe (1896)	C = 52.2	H = 3.1
Thoms (1906)	C = 51.94—55.72	H = 3.44—4.76
Dekker (1906)	C = 52.3	H = 3.9
Manning (1910)	C = 52.3	H = 3.4

Herzig and collaborators have recently (1905—1909) proposed for Methylotannin, a substance obtained by methylation of tannic acid with diazomethane, the following two formulae: $C_{24}H_8O_7$ $(OCH_3)_8$ or $C_{25}H_{10}O_7$ $(OCH_3)_8$, which would represent tannic acid as $C_{24}H_{16}O_7$ or $C_{25}H_{18}O_7$. Feist (1909) regards tannic acid as $C_{27}H_{22}O_{17}$ or $C_{27}H_{24}O_{18}$, and Manning (1910), who has prepared Ethyl Tannate $C_{41}H_{27}O_{21}$ $(OC_7H_5)_5$, gives it the formula, $C_{41}H_{32}O_{26}$.

The first attempts to give a constitutional formula to tannic acid date back to Schiff (1870), who claimed to have obtained digallic acid (tannic acid) on treatment of gallic acid with

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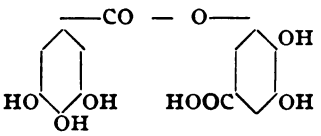
arsenic acid. This product is known in chemical literature as α or Schiff's digallic acid. It has also been prepared by Walden (1898), Geschwender (1906), and Nierenstein (1907). Iljin (1906—1910) and also Biginelli (1909—1910) consider it to be a mixture of a number of organic arsenic compounds, which view is not supported by Nierenstein (1906—1910). Two more digallic acids have been prepared, one by Böttinger (1884) and one by Emil Fischer (1908), but neither of these compounds seem to be identical with the digallic acid isolated by Nierenstein (1910) from tannic acid.

Schiff represented tannic acid as digallic acid



which formula lived happily until 1890, when Flawitzki discovered that tannic acid is optically active, which, of course, did not agree with this digallic acid formula. Though this discovery of Flawitzki was quite original, the fact that tannic acid is optically active has been known to Scheibler (1866), van Tieghem (1867), and Seyfart (1869). Flawitzki's observation has since been confirmed by Günther (1895), Walden (1897), Rosenheim and Schidrowitz (1898), Dekker (1906), Nierenstein (1909), and Iljin (1909).

Further evidence against the digallic acid formula was brought forward by Walden (1897—1898), who showed that it differed from Schiff's digallic acid with regard to its absorption of light and electrical conductivity. Whereas digallic acid conducts the electric current, tannic acid does not do so.[1]

More evidence was brought forward against the digallic acid formula by those workers who estimated its molecular weight. The following data were obtained:—

Paterno (1889), in water	M. W.	2630—3700
Isabonajeff (1890), in acetic acid	"	1322
Walden (1898), in acetone	"	1500
Krafft (1899), in water	"	1587—1626
Paterno[2] (?), in alcohol	"	322
Iljin (1910), in acetone	"	1247—1637

[1] I notice that "White and Jones" (Jour. Amer. Chem. Society, 1910) have recently shown that tannic acid does conduct the electric current.

[2] Quoted from Schröder, Zur Kenntnis des Gerbprozesses (Dresden, 1909).

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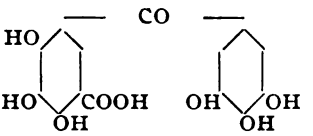
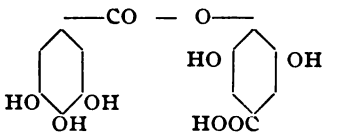
The M. W. of digallic acid is 322.

Schiff's digallic acid formula was followed in 1884 by a formula of Böttinger:—



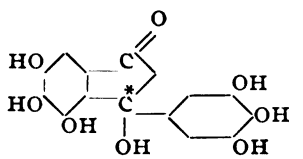
which had the same disadvantage as Schiff's formula with the addition of one more, for it contained six hydroxyls, whereas tannic acid contains only five (Trimble, Löwe, Nierenstein, and others), or according to Herzig and Tscherne (1905) four such groups.

Vournassos (1903) suggested for tannic acid:—



and succeeded in obtaining a nice crystalline benzoyl derivative of tannic acid.

Most valuable work on the chemistry of tannic acid was done by Dekker (1906), who suggested the following formula:—



This formula fully explains the optical activity of tannic acid, and also shows why tannic acid does not conduct the electric current. However, as it was pointed out by Nierenstein (1906—1908), it has the following disadvantages:—(1) It contains seven hydroxyls, whereas tannic acid has only five such groups; (2) it ought to have tinctorial properties, whereas tannic acid shows only dyeing properties when heavy mordants such as titanium are used; and (3) it does not explain readily (if at all) the transformation of tannic acid into ellagic acid,[1]) viz:—

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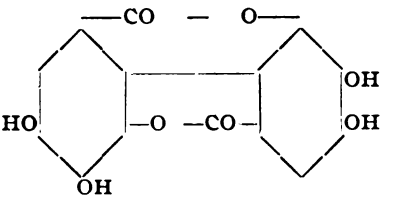
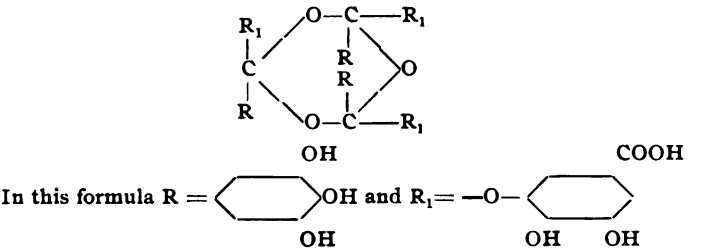
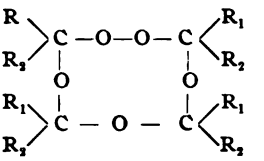


Two more formulae have been proposed, one by Lloyd (1908):



The second formula has been proposed by Iljin (1909):



where $R^1 = -CO.C_6H_2(OH)_3$ and $R_2 = -C_6H_2(OH)_3$.

It is, however, unnecessary to comment on these formulae.

I now turn to my own work on the subject, which was started in 1903 and is still in progress. I have been led to the conclusion that tannic acid is a mixture of at least two compounds, namely, digallic acid (tannic acid) and leucotannic acid. My results are expressed in the following résumé and in the table given on the next page:—

(1) Acetylated tannic acid (m. p. 146°) consists of two compounds, one melting at 203—206° (penta-acetyl digallic acid) and a second melting at 166° (penta-acetyl leuco-tannic acid).

(2) Penta-acetyl digallic acid can be converted on reduction into penta-acetyl leuco-tannic acid.

[1] The formation of ellagic acid from tannic and gallic acid was known to Chevreuil and also to Braconnot (1828). The latter suggested the German name "Ellag" which is the reverse of "Galle."

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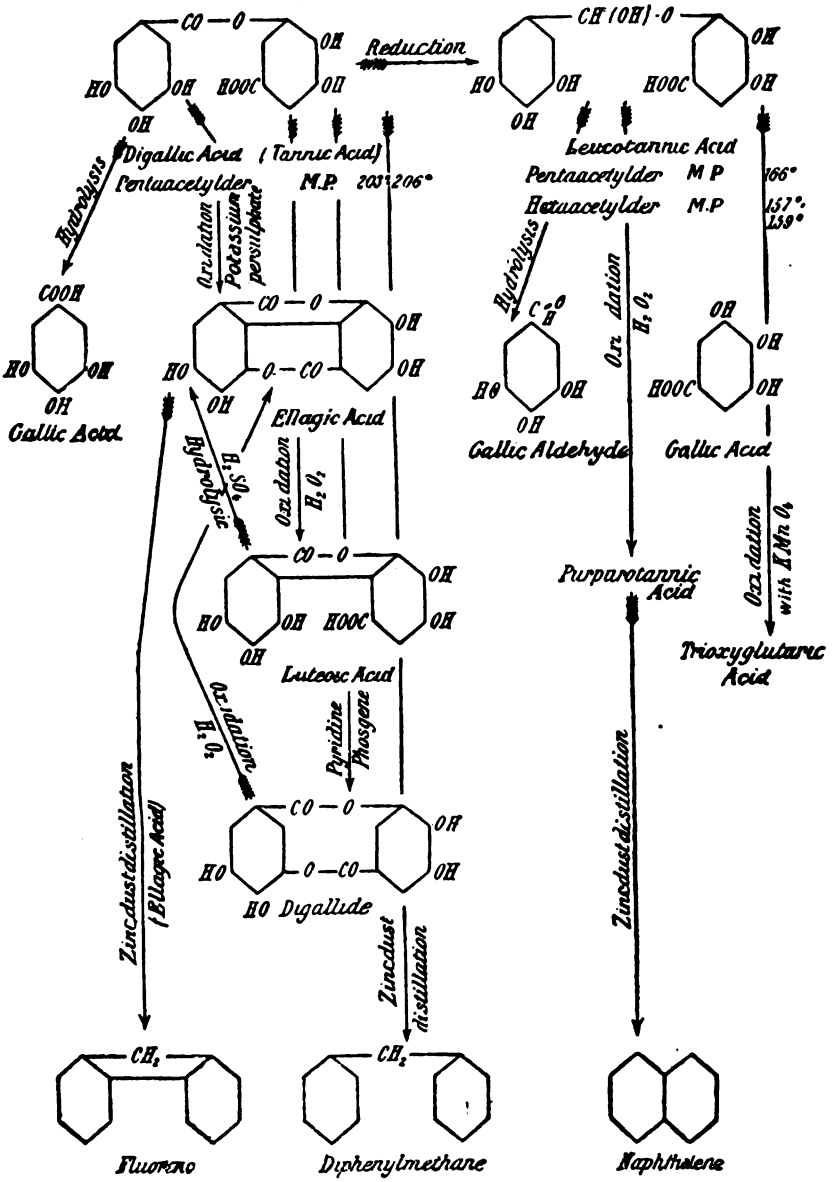

(3) Penta-acetyl leuco-tannic acid can be further acetylated when hexa-acetyl leuco-tannic acid (m. p. 157—159°) is formed.

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(4) Penta-acetyl digallic acid cannot be further acetylated.

(5) Penta-acetyl digallic acid forms on oxidation with potassiumpersulphate and sulphuric acid, ellagic acid.

(6) It also forms when oxidized with H_2O_2 luteoic acid, which can be transformed on hydrolysis into ellagic acid.

(7) Penta-acetyl digallic acid forms when treated with phosgene the corresponding digallide which can be converted on oxidation with H_2O_2 into ellagic acid.

(8) Ellagic acid obtained from tannic acid yields fluorene on zinc dust distillation.

(9) Penta-acetyl leuco-tannic acid gives on hydrolysis gallic acid and gallic aldehyde, whereas penta-acetyl digallic acid only forms gallic acid.

(10) Penta-acetyl leuco-tannic acid further yields on oxidation not ellagic acid but a red product, purpuro-tannic acid.

(11) Purpuro-tannic acid yields naphthalene on zinc dust distillation.

(12) Penta-acetyl leuco-tannic acid gives on oxidation with $KMnO_4$ trioxyglutaric acid.

(13) Tannic acid forms diphenylmethane on zinc dust distillation.

(14) I further obtained the inactive digallic acid from tannic acid. It was prepared by several carboethoxylations of tannic acid on treatment with pyridine. It crystallized from dilute alcohol and melted at 268—270.° The penta-acetyl, penta- benzoyl, and penta-carboethoxyl digallic acids were also prepared.

(15) The penta-acetyl digallic (m. p. 211—214°) which was inactive, forms on reduction and acetylation the inactive hexa-acetyl leuco-tannic acid (m. p. 154—155°), which is readily split into *l*-hexa-acetyl leuco-tannic acid (m. p. 151°) and *d*-hexa-acetyl leuco-tannic acid (m. p. 153—154°).

This makes it reasonable to conclude that tannic acid (Tanninium lev. pur. Schering) consists of at least two compounds, and is not a simple substance.

DISCUSSION.

Professor Knecht said the lecturer had given a concise historical survey of the chemistry of tannic acid, and had explained

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his own interesting views of the subject of its constitution. The observation of Humphrey Davy of the very small increase in the boiling point brought about by the solution of tannic acid in water had been confirmed by others. He had recently had occasion to repeat the experiment in a Beckmann ebullioscope which he had devised and which was heated by electricity. The boiling point of the solution, its non-conductivity for the electric current, and the fact that is showed a luminous beam when light was passed through it, showed that tannic acid belonged to the colloids. In all text books, however, Schiff's formula was given. He scarcely thought that Dekker's formula could be accepted as it would represent tannic acid as being a pronounced mordant color. Had the lecturer referred to the work of Pliny on tannic acid?

Dr. Engler said he should like to have heard something about the application of tannic acid.

Mr. Vlies said he did not agree with the lecturer's definition of a tannin. One of the substances precipitated by gelatin was formaldehyde, and he asked the lecturer if he carried the definition so far as to include this substance. In the preparation of gallamide he had found that tannin gave a better yield than gallic acid when treated with ammonia. He would be glad if Dr. Nierenstein could give an explanation of this.

Professor Knecht mentioned that another fallacy which a great many people considered in the other light was that tannic acid precipitated the basic colors, and gallic acid did not. All the basic colors on the market were completely precipitated in presence of sodium acetate by both tannic and gallic acids. He asked the lecturer whether he could throw any light on the chemistry of the tannin discharge style used in calico printing.

The Lecturer said that the Chairman had expressed the opinion that tannic acid was a colloid in aqueous solution and a crystalloid in alcohol with a molecular weight about 3,000. This was borne out by the work of Schroeder. He had referred to the work of Pliny in his paper. Sisley had shown that by merely oxidizing tannic acid in open dishes only ellagic acid was formed.

In reply to Dr. Engler, the Lecturer said that he considered

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that telling Manchester people about the application of tannic acid was like taking coals to Newcastle. With regard to other applications, he mentioned a book by Hinrichsen on the manufacture of ink, which contained a great deal of reliable and useful information on the subject. With regard to the question raised by Mr. Vlies, the Lecturer said that he still held to his definition of a tannin material. Formaldehyde was used on the large scale for tanning leather.

ABSTRACTS.

Crude Glycerine; Analysis of ——. Report by O. HEHNER, J. ALLAN, J. B. MCARTHUR, W. H. PHILLIPS, P. TAINSH, F. TATE, and J. L. BUCHANAN. Jan. 31, 1911.[1]—A general meeting of makers of crude glycerine, held in London on July, 1909, resolved that it was desirable to standardize the tests of crude glycerine, and appointed a committee to make investigations and report. The expert committee has been able to work in conjunction with similar committees in America, France, and Germany, and the methods detailed have their unanimous support, and are recommended as international standards.

Sampling.—A sampler has been devised with the object of overcoming the objections to the glass tube usually employed. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the sampler is filled almost instantaneously with the glycerine. There are also a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two and then closed. After withdrawing the sampler, the sample is discharged into the receiving vessel by opening the ports. When the drum contains settled salt, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum, and it is therefore recommended that the drum should be sampled before the salt has settled. A mutually approved person shall sample with the sectional sampler, then seal the drums, brand them with a num-

[1] J. S. C. I., May 14, 1911.

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ber for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted, and a report of same made in the certificate, together with the temperature of the glycerine. Each drum must be sampled.

1. *Determination of free caustic alkali.*—Weigh 20 grams of the sample into a 100 cc. flask, dilute with approximately 50 cc. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 cc. of phenolphthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 cc. of the clear liquid, and titrate with N/1 acid. Calculate to percentage of Na_2O existing as caustic alkali. 2. *Determination of ash and total alkalinity.*—Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerine over a luminous argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilization and the formation of sulphides. When the mass is charred to the point that water will not become colored by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled water and titrate total alkali, using as indicator methyl orange cold, or litmus boiling. 3. *Determination of alkali present as carbonate.*—Take 10 grams of the sample, dilute with 50 cc. of distilled water, add sufficient N/1 acid to neutralize the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water free from carbon dioxide, and titrate back with N/1 sodium hydroxide, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the alkali found in (1). The difference is the percentage of Na_2O existing as carbonate. 4. *Alkali combined with organic acids.*—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids. 5. *Determination of acidity.*—Take 10 grams of the sample, dilute with 50 cc. of distilled water free from carbon dioxide, and titrate with N/1 sodium hydroxide and phenolphthalein. Express in terms of Na_2O required to neutralize 100 grams. 6. *Determination of total residue at* 160° C.—For this determination the crude glycerine should be slightly alkaline with sodium carbonate, not exceeding the equivalent of 0.2 per cent. of Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerols this alkalinity must not be exceeded. Ten grams of the sample are weighed into a 100 cc. flask, diluted with water and the calculated quantity of N/1 hydrochloric acid on sodium carbonate added to give the required degree of alkalinity. The flask is filled to 100 cc., the contents mixed, and 10 cc. measured into a weighed Petrie or similar dish 2.5 in. diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue, a smaller quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 milligrams. The dish is placed on a water-bath (the top of the

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160° C. oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate ¾ in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerine is placed. If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° C. can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapor is seen to come off, the dish is removed and allowed to cool. An addition of 0.5 to 1 cc. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours is required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then heated again for one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1.5 mgrms. per hour is obtained. *Corrections to be applied to the weight of the total residue.*—In the case of acid glycerines a correction must be made for the alkali added. 1 cc. to N/1 alkali represents an addition of 0.022 gram. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the sodium hydroxide and carbonate to chloride. The corrected weight, multiplied by 100, gives the percentage of total residue at 160° C. Preserve this residue for the determination of the non-volatile acetylizable impurities. 7. *Organic residue.*—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. It should be noted that alkali salts of organic acids are converted to carbonates on ignition, and that the CO_3 radical thus derived is not included in the organic residue. 8. *Moisture.*—Two to three grams of very pure bulky asbestos freed from acid-soluble material which has been previously dried in a water oven is placed in a small stoppered weighing bottle of about 15 cc. capacity. The weighing bottle is kept in a desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1.5 grams of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about 48 hours. At lower temperatures the

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test is prolonged. The sulphuric acid in the desiccator must be frequently renewed.

Acetin process for glycerol determination.—This process is the one agreed upon at a conference of delegates from the American, British, French and German Committees, as the process to be used (if applicable) whenever only one method is employed. On pure glycerins the results are identical with those of the bichromate process. For its application the crude glycerine should not contain over 50 per cent. of water. *Reagents required.*—(*A*)—*Best acetic anhydride.* This should be carefully selected. A good sample must not require more than 0.1 cc. of N/1 NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank. (*B*)—*Pure fused sodium acetate.* The purchased salt is completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous. (*C*)—*A solution of caustic soda for neutralizing, of about* N/1 *strength, free from carbonate.* This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required. (*D*)—N/1 caustic soda, free from carbonate. Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected. (*E*)—*N/1 acid.* (*F*) *Phenolphthalein solution.* Dissolve 0.5 per cent. of phenolphthalein in alcohol and neutralize the solution.

Method of Analysis.—Into a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerine. Add first about 3 grams of the anhydrous sodium acetate, then 7.5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside. The flask is connected with the condenser by either a ground glass joint(preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor. Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask. Allow the flask to cool somewhat and through the condenser tube add 50 cc. of the distilled water, free from carbon dioxide, heated to about 80° C., taking care that the flask is not loosened from the condenser. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until the solution is complete except a few dark flocks resulting from organic impurities in the crude glycerine. Cool

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flask and contents without loosening from condenser. When quite cold, wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask. Filter the contents of the flask through an acid-washed filter into a Jena-glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (F), then run in a caustic soda solution (C) or (D) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached, the sides of the flask are washed down with water free from carbon dioxide, and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained. Now run in from a burette 50 cc. or a calculated excess of N/1 sodium hydroxide (D), and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of alkali with N/1 acid (E) until the pinkish yellow, or chosen end point color just remains. A further addition of the indicator at this point will cause a return of the pinkish color; this must be neglected, and the first end point taken. From the N/1 sodium hydroxide consumed, calculate the percentage of glycerol, after making the correction for the blank test described below. 1 cc. of N/1 sodium hydroxide = 0.03069 gram of glycerol. The coefficient of expansion for N/1 solutions is approximately 0.00033 per cc. for each degree C. A correction should be made on this account if necessary. As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralizing the acetic acid, it is not necessary to add more than 5 cc. of the N/1 alkali (D) as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination. *Determination of the glycerol value of the acetylizable impurities.*—The total residue at 160° C. is dissolved in 1 or 2 cc. of water, washed into a clean acetylizing flask of 120 cc. capacity and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determination before described. Calculate the result to glycerol.

Bichromate process for glycerol determination. Reagents required. (*A*)—*Pure potassium bichromate* powdered and dried in air free from dust or organic vapors, at 110° C. to 120° C. This is taken as the standard. (*B*)—*Dilute bichromate solution.* 7.4564 grams of the above bichromate (A) are dissolved in distilled water and the solution made up to one liter at 15.5° C. (*C*)—*Ferrous ammonium sulphate.* Dissolve 3.7282 grams of potassium bichromate (A) in 50 cc. of water. Add 50 cc. of 50 per cent. (by volume) sulphuric acid, and to the cold

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undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate. (D)—*Silver carbonate.* This is prepared as required for each test from 140 cc. of 0.5 per cent. silver sulphate solution by precipitation with about 4.9 cc. of N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant and wash once by decantation. (*E*)—*Subacetate of lead.* Boil a pure 10 per cent. solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide. (*F*)—*Potassium ferricyanide.* A very dilute solution containing about 0.1 per cent. *Method of analysis.*—Weigh 20 grams of the glycerine, dilute to 250 cc. and take 25 cc. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 cc. and then add 0.15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 cc., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 cc. is ample.) Occasionally a crude glycerine will be found requiring more, and in this case another aliquot portion of 25 cc. of the dilute glycerine should be taken and purified with 6 cc. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate. Measure off 25 cc. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add first 12 drops of sulphuric acid (1:4) to precipitate the small excess of lead as sulphate, then 3.7282 grams of the powdered potassium bichromate (A). Rinse down the bichromate with 25 cc. of water and allow to stand with occasional shaking until all the bichromate is dissolved. Now add 50 cc. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol. 1 gram of glycerol is equivalent to 7.4564 grams of bichromate; and 1 gram of bichromate to 0.13411 grams of glycerol. *Notes.*—(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to. (2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process. (3) For crude glycerine practically free from chlorides the quantity of silver

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carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 cc. (4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

Instructions for calculating actual glycerol content.—(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any be present. (2) Determine the total residue at 160° C. (3) Determine the acetin value of the residue at (2) in terms of glycerol. (4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

Notes and recommendations.—Experience has shown that in crude glycerine of good commercial quality, the sum of water, total residue at 160° C., and corrected acetin result comes to within 0.5 of 100. Further, in such products the bichromate result agrees with the uncorrected acetin result to within 1 per cent. In the event of greater differences being found, impurities such as polyglycerols or trimethyleneglycol are present. Trimethyleneglycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the "spread" between the acetin and bichromate results of such distillates. Trimethylene-glycol shows by the former method 80.69 per cent. and by the latter 138.3 per cent. expressed as glycerol. In valuing crude glycerine for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

Recommendations by Executive Committee.—If the non-volatile organic residue at 160° C. in the case of a soap lye crude glycerine be over 2.5 per cent., *i.e.*, when not corrected for carbon dioxide in the ash, then the residue shall be examined by the acetin method, and any excess of glycerol found over 0.5 per cent. shall be deducted from the acetin figure. In the case of saponification, distillation and similar glycerins, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent., the organic residue must be acetylated, and any glycerol found (after making the deduction of 0.5 per cent.) shall be deducted from the percentage of glycerol found by the acetin test.—J. A.

Leather; the Weighting of ——. F. Abraham. *Chem. Zeit.*, 1911, **35**, 453[1].—Weighting materials have been used on leather for 50 years, and Eitner drew attention to the practice 25 years ago. The importation of American hemlock-tanned leather and English leather into Germany began about 50 years ago, and the goods were characterized by their cheapness and fine appearance. High duties on the imported goods were demanded, but were found unnecessary, as the leather when put into manufacture was found to be no cheaper than the home-tanned product.

[1] Through J. S. C. I.

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The imported leather contained materials added solely for the purpose of weighting, and the consequent lowering of prices forced the home tanners to resort to similar devices, especially with leather for export. Water and tannin are too easily removed to be used as weighting materials, and an excess of the latter causes brittleness. Sugar is used to a great extent; it is found to the extent of 2 per cent. in unweighted vegetable-tanned leather. It is used in the form of grape or starch sugar or syrup, molasses or dextrin, and applied in strong solution to the flesh side of the damp leather. Bad results were first obtained until the English custom of drying the leather quickly at 50° C. was followed, by means of which the leather does not remain damp. Of mineral weighting agents, magnesium sulphate and barium chloride are the most common. In a recent case a belting firm who had obtained their leather for a long time from one leather works suddenly asserted that the leather contained 10 per cent. of sugar, and reduced their payment for it by a corresponding amount. The leather manufacturers complained and took the case to law, when it was decided that the belting makers had no right, on judicial grounds, to reduce their payments. The leather on analysis showed 6 per cent. of sugar, and the leather makers stated that their product was so specifically light that the addition was necessary to make it saleable, although Paessler showed that other specimens of leather for the same purpose were specifically lighter. The court could find no evidence of fraud, for the seller could assume, as the goods had been accepted for years without any objection, that the buyer was aware of the added weighting material, seeing that the value of the goods was M. 185,000, while an analysis would cost M. 8 only. In the evidence it was stated that sugar and barium chloride were harmful to health, owing to their attraction for water, and damaged the leather, but this was denied. Instances were given in which magnesium and aluminium sulphate were introduced into the leather owing to these substances having been used for clarifying the liquors. The chemical analysis was of as much importance to the seller as to the consumer. D. J. L.

Semi-Chrome Tanned Leather. *Leather Trades Review,* March 15, April 19, May 15, 1911.—East India leather, particularly kips and heavy calf, is used for this combination tannage. The skins are soaked, then shaved or split and then partially detanned by drumming in a warm solution containing soda to the amount of 1½ to 2 per cent. of the weight of the shaved skins, or borax, 2 to 2½ per cent. of the weight of the skins. The alkaline solution should be added slowly and the drum kept in constant motion to avoid stains, the time being from 30 to 45 minutes. The leather is then washed in the wheel in warm water from 20 to 30 minutes. Any excess alkali is then neutralized, preferably with an organic acid, and the leather again washed.

The chroming is done in a drum, any good one-bath chrome liquor being used. The temperature during this process should not exceed 80° F. After chroming, the stock is neutralized with soda or borax, and again washed.

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To color black, the leather may be dyed blue and then brushed on the gram side with black dye. For brown shades, sumac or fustic may be used as a mordant, followed by an aniline dye. For light shades, acid dyes are preferred. A good recipe for medium brown is, for 100 lbs. leather, azoflavine R. S., ¼ lb., acid brown, R. ½ lb., dark brown, ½ lb. Dissolve in hot water and add ¾ to 1 pint formic acid. For dark brown, to 100 lbs. leather, rheonine, A. L., ¾ lb., vesuvine, ¼ lb. Dissolve in hot water, (140° F.) and add a little acetic acid. Drum the leather in this for 20 minutes and add a weak solution of cotton blue, B. B. to tone down to the shade required.

The next process is fat-liquoring, blacks requiring more oil than browns. For 100 lbs. black leather use 2½ lbs. neatsfoot oil and 2½ lbs. soft soap or Marseilles soap. The dissolved soap is added to the oil slowly, with stirring. A small quantity of Irish moss helps emulsification. If a dull finish is required, twice as much soap is used. For colored leathers, turkey red or other sulphonated oil is used, with egg yolk. For each 100 lbs. leather, 1½ lbs. Turkey red oil and ¼ lb. egg yolk, emulsified in hot water, are used.

The leather after horsing up for a day is next "struck out" to remove surplus water, etc. After hanging for a time, it is "set out," so that when dry it may have a fine smooth surface. It may be dried either by hanging or tacking out. The former method is better if soft pliable stock is desired.

When thoroughly dry the leather is taken down and "staked" by hand or machine. This process makes the leather lie flat, opens the pores to receive the finishing dyes, raises a nap on the flesh side and increases the pliability and softness of the leather.

For "box" finish, the black color may be given by iron liquor and levant ink or by an aniline dye, it being an undecided question which method is best. The objection to iron is a tendency to brittle grain caused by oxidation. This defect may be remedied by a logwood mordant.

Logwood extract, crystals ..... ½ lb.
Fustic extract ..... ¼ lb.

Dissolve in 2 gallons hot water. When cool, brush over the grain and then apply a commercial iron liquor, or 4 ounces copperas and 2 oz. blue vitriol in 1 gallon hot water. After the iron liquor give a good coating of levant ink, and dry. Then "season" with ox blood or albumen paste to which a little milk and levant ink are added. Dry and glaze by hand or machine.

New Bating Materials. W. EITNER. *Der Gerber,* April 1 and 15, 1911. —The purpose of dung bates is to cleanse the unhaired hide from lime and accompanying substances. They also promote the liquefaction of a portion of the hide, a necessary condition for softness; and in the case of some kinds of leather they cause or promote elasticity. Finally, the bates loosen up the fibers of the hide and so aid in the absorption of tanning materials, and the fillings used in making enamelled leathers.

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It is now well known that other agents delime better than bates, so that if deliming only is wanted, dung bates are no longer used. The deliming is done by neutralizing the lime in the hide with an acid forming a neutral salt which is easier to wash out than the lime. The washing out of these salts is promoted by the fact that the hide "falls" when the alkalinity of the lime is neutralized.

Of simple deliming agents which may be classed as bates, that longest in use in sugar. Honey or very sweet fruit has long been used in the East in the manufacture of morocco leather. The sugar makes a soluble compound with the lime, and this compound is washed out. Excess of sugar is not injurious, as excess of acid often is. A number of acids form soluble calcium salts. Among these pyroligneous acid which because of its slight solubility in cold water cannot be used in excess, and in spite of its high price it is used for some purposes. For the heavier kinds of leather kresolsulphonic acid, called anticalcium, was much used because of its cheapness and antiseptic properties.

Hydrochloric, acetic and lactic acids are used for deliming, the last by chrome tanners. A recent rival of lactic acid is formic acid, for which special properties are claimed. The latest addition to the list is butyric acid, which has been hailed as the best agent for deliming, and is recommended for use in the soaking of dry hides, and for plumping and pickling. Because of its solvent action on the hide it gives a smooth and slippery grain, and the writer thinks it will be found too wasteful of hide-substance for economical use.

The quantity of acid necessary for deliming depends on the lime content of the hide, on the kind and concentration of the acid used and on the duration of the process. An average of 10-12 grams HCl (commercial solution) per 1,000 grams of white hide is suggested.

A further use of bates is the so-called liquefaction of the hide, which consists in the removal of dirt and the separation or loosening of the hide fibers. The substances removed include the remaining hair and the contents of the hair follicles, which would decay and cause trouble. Besides these a larger quantity of material is removed, consisting of dissolved or swelled hide-substance. This latter material is only removed in the case of upper leathers. In the case of sole leather the object is to precipitate it with acid and leave it in the hide. The removal of the interfibrillar substance in the case of upper leather is accomplished partly by the chemical-physiological processes set up by the bate, and partly by the mechanical effect of manipulation. There are some differences in the effect of bates made from dog-dung and hen-dung. The latter is "sharp" in its action, causing the hide to "fall" quickly and become smooth; dissolving less hide substance than the other. When the leather must be soft it has to be worked in a wheel. The dog dung-bate has greater solvent power and is used for glove and other very pliable leathers. The cause of these differences is to be found in the different character of the fermentations set up by the two kinds of bates, resulting in different fermentation products.

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For a long time tanners have wished to avoid the use of dung bates because they sometimes act abnormally with bad results; because they cause complaints on the part of the neighbors and the health authorities, and because they are becoming increasingly dear. A number of substitutes have been devised, some of which have proved fairly satisfactory.

The natural bating materials differ, much in their effects, the dog-dung bate being used for the elastic glace leather, and the hen-dung bate for upper leather made from the hides of cattle, which must be tough but not easily stretched. Bran bates, by means of fermentation, loosen the hide fibers, and cause less change of the hide substance than the dung bates.

As a substitute for dog-dung, "phosphor-butyralin" is offered, made by fermentation of refuse from the manufacture of glucose. It contains free butyric acid and butyrates and phosphates of ammonia, and many ferments producing acid fermentation.

A bate is made from fleshings by boiling it with a little soda and allowing the resulting bouillon to ferment, either by germs from the air, or by adding a small amount of dog-dung. This bate must be made fresh often because it soon decays. It is used in tanning calf-skins and various sorts of vache leather.

The efficient agent in "oat-straw" bate is the *bacillus subtilis*. It may be made by inoculating gelatine solution with water in which hay has been steeped. This bate works well for both chrome and bark leather, and for goat skins. Its action is somewhat slower than the dung bates, but it is less liable to go wrong. A mixture of bran and dung bates is often used; several such have been patented.

A bate which has been in successful use for some years is the "erodin" of Popp and Becker. It is made by adding to ground meat, dog-dung and soda, permitting the mass to ferment and then adding talcum and guano, The mass is then dried and ground. For use it is mixed with warm water.

The sale of erodin for ten years shows that artificial bates are here to stay. Their sale is promoted by the increasing scarcity of dog-dung, which has even been imported from Constantinople.

Another artificial bate is "oropon," a yellow powder made from the dried and powdered pancreas of cattle, to which ammonium chloride is added in considerable quantity to maintain an alkaline reaction. Oropon is another kind of bate, possessing in a higher degree than dog-dung solvent power toward hide substance and loosening effect on the hide fiber, bringing about a kind of digestion. The pancreatic juice is not a homogeneous body, but contains trypsin, splitting up albumen, the diastatic ferment which digests starch and carbohydrates and a fat-splitting ferment. Like dung bate oropon does best at 34° C. (93° F.) and when feebly alkaline. At 60° C. it ceases to work.

Another artificial bate called "Esco" has for a basis vegetable albuminous material. It is a brown powder with a strong smell. Its

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effect is comparable to a mixture of hen-dung and bran bates. A combination of oropon and esco has given good results for colored calf.

A preparation called "diastophor" serves both as a bate and filler. It is a thick extract made from the germs of grain, and has a fermenting effect on starch and some other carbohydrates. L. B.

The Filter and Shake Methods. F. J. KOPECKY; B. KOHNSTEIN. *Ledertechn. Rundschau*, 1911, 121-3.—At a meeting of Austrian leather industrialists, Herr Kopecky gave a historical resumé of the hide powder methods. The original method by Weiss and Simand (1886) at Vienna was really a shake method and was improved by Procter (1887) who introduced the filter. The filter method was adopted as official in 1897 at the first Congress (London) of the I. V. L. C. The original method was improved in America and became there official. At the International Congress at Brussells, 1908, the shake method which had been so thoroughly worked out in America, was chosen as the standard; the German extract makers still adhere to the filter method. A great advantage of the shake method is its suitability for factory control of which the central laboratory at Ridgway, Pa., offers a striking example.

Prof. Kohnstein referred to the advantage of chroming. White hide is easily fermented and unsuited to the analysis of used liquors. The filter method is more liable to give variable results. W. J. K.

The Chemistry of Resins. GEORG GRASSER. *Collegium*, 1911, 148-50.—The author reports the results of general tests made upon the resins commonly used in the manufacture of lacquered leather. Copal (kauri copal is most employed) has sp. gr. 1.08-1.17 and contains 60-70 per cent. of resin acids which dissolve in alkali; the solution on treatment with metallic salts, throws down compounds which are soluble in turpentine oil, linseed oil, etc., used as varnishes. The chlorhydrins, amyl alcohol, and amyl acetate are good solvents for copal while chloroform, ether, alcohol, acetone and petroleum ether dissolve it with more difficulty. It softens at 200°, is wholly liquid at 250°; 25 per cent. light colored distillate collects at 240-260°, 30 per cent. more at 260-280° and 10 per cent. at 280-335° with darkening. Colophony from *Pinus resinosa*, has sp. gr. 0.81, is easily soluble in alcohol, etc., and miscible with fat oils on fusion. Eighteen per cent. volatile matter was obtained by vacuum distillation; residue, m.p. 84-86°. The resin acid obtained by saponification had a melting-point of 96°. Dammar resin from Borneo contained 80 per cent. saponifiable. Elemi a soft resin contains 8 per cent, ethereal oil and the residue is mostly volatile on dry distillation. The resin does not readily saponify. W. J. K.

The Testing of Tannin Extracts. (Continued.) A. GANSSER. *Collegium*, 1911, 177-80.—Additional (ante p. 322) results are reported showing the comparative effect of various extracts (special local brands) upon the absorption by gelatine-coated cotton. The general conclusion is that easily soluble tanstuffs are fixed the least. The nature of the resins greatly affects the results.

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The addition of non-tans such as molasses glucose and gallic acid, had little effect upon the absorption. W. J. K.

Meeting of the German Section of the I. A. L. T. C. *Collegium*, 1911, 193-8. Dr. Fahrion gave an address on neatsfoot oil, its analytical constants and adulterations; this will be printed later. In the discussion, Wegner recommended the color reactions, Auerbach the constants.

Dr. Auerbach reported concerning extraction apparatus. One hour (official) is too short a time for complete extraction. The Teas apparatus effects complete extraction and gives good results but is too dear. Koch's apparatus is not practical. Grasser's extractor (abstract this JOURNAL, 5, 526) is of copper, hence not always suitable. An improved form of glass, Grasser-Allen, costing 5 marks, will be described later. Hr. Wegner described an improvement in Koch's apparatus, consisting in leading away the delivery tube side ways, instead of upward through the stopper.

The following table gives parallel results obtained by different analysts during a visit of two German chemists to Leeds:

NON-TANS IN CHESTNUT EXTRACT.

	Blank		Non-tans per cent.		
	Paessler	Abraham	Paessler	Abraham	Procter (or assts.)
Hide powder white, American.	5.6	4.8 mg.	10.49	10.49	9.96
Freiberg	6.8	2.6	11.22	10.92	11.80
Freiberg, light chrom.	9.8	9.8	10.63	10.54	10.44
Zeuthen's method	3.4	2.4	10.95	10.83	10.44

In Procter's laboratory the visitors found some working details simplified. The hide powder is chromed by swinging (Schwenken) with the solution either by hand or slow rotating apparatus. The solution is first diluted with 10 parts water, then added, giving a uniform chroming. A coarse linen cloth is used in washing; the hide can be removed almost quantitatively. The kaolin is not added direct, but the detanned liquor is strained onto the kaolin in a beaker, mixed and then filtered. Parker's laboratory in London was also visited. The final consensus, including the report of Dr. Jablonski, who also visited England was that the shake method is worked in Germany exactly as in England and as well; the Englishmen have the advantage of experience.

Dr. Auerbach called attention to the differences in insoluble determinations; too long filtration may alter the solution. He found that a kaolin already used filtered rapidly and gave almost always a clear solution.

Dr. Veit stated that reports from different laboratories of sugar in quebracho extract varied greatly; an official method is desirable. Dr. Philip considered von Schroeder's method for glucose accurate; unification on the strength of acid used for inversion is desirable. Kohnstein's method gives variable results. The question was referred to the German Analysis Commission.

Prof. Becker spoke on disinfection of hides and referred to recent

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publication upon the subject. He had experimented upon the following mixtures and solutions: (1) slaked lime = 2 k. lime, 5 l. water (2) 2 k. lime, 100 g. red arsenic, 10 l. water (3) residue of 2 + 10 per cent. Na_2S (4) lime liquors 2 days old (5) lime sediment (fertilizer) (6) cryst. Na_2S (7) red arsenic. The anthrax bacilli grew further in all these, but entirely lost their virulence and no longer killed mice on inoculation. In former years he had successfully employed mustard meal in sterilizing vat and pit liquors. He now finds that an 0.05 per cent. solution of mustard oil will kill anthrax spores in 5 minutes. An alkaline solution of dibrom β-naphthol rapidly kills the spores but would discolor the leather. This is a preliminary report, the subject being still under investigation. W. J. K.

The Behavior of Tannin Towards Albumin and Metallic Salts. GEORG GRASSER. *Collegium*, 1911, 185-92, 199-200.—As reagents, 20 per cent. solutions of gallotannic acid, egg white and the respective metallic salts (including free I and Br) were employed, diluting 1:100 for reaction. The tannin and salt solutions were first mixed in equivalent amounts (tannin reckoned dibasic, 1.6 g. = 1.7 g. $AgNO_3$), giving generally water soluble compounds; on adding, however, the albumin, precipitates were obtained containing all three reagents. The reaction was completed by heating, the precipitates washed, dried and analyzed with the following percentages:

		Albumin	Tannin (by difference)
Ag	18	32	50
Bi	14	40	46
Hg	15	50	35
Zn	10	48	42
Cu	9	50	41
Pb	16	45	39
Fe	5	60	35
V	6	60	34
Br	15	21	64
I	23	21	56

The vanadium compound was obtained by adding the albumin first to NH_4VO_3 (no ppt.) and the tannin last. The albumen was determined by the Kjeldahl process. These compounds are characterized by a low content of metal, preponderance of albumin and a roughly constant amount of tannin. Probably by varying the reaction conditions, different compounds would result. The author finishes with a detailed table of the reactions of 8 familiar vegetable tanning materials with mineral salts + albumin. In general the results vary more with the tanstuff than the reagent but they are not characteristic enough for systematic identification. W. J. K.

Process for Box Calf. MAGYAR BORIPAR through *Ledertechn. Rundschau*, 1911, 76-7. To obtain the desired fine grain, together with full-

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ness, the single-bath process is suited, if preceded by a pickle and followed by a "nourishment" like that used with glove leather. Arsenic is used in liming, 1 kg. to 100 kg. dry hide with the necessary amount of lime. After 3-4 days a fresh white lime is used, bettering the 2d. or 3d. day. After unhairing, bran bating, etc., follows 20 minutes drumming with a pickle of 50 grams salt, 5 grams HCl, 5 grams alum sulphate, 1 gram spirits turpentine, 5 l. water to every kilo of pelt. For tanning, 100 k. pelt, 25 k. chrome alum are dissolved in 200 l. water and 8.75 k. cryst. soda in 22.5 l. water. This is gradually applied until the tanning is complete. For deacidifying, 1 k. borax is used. After skiving a mixture of 20 lbs. wheat flour, 4 l. egg-yolk, 45 lbs. salt solution is applied for ¾ hour. A logwood-iron blacking is used. W. J. K.

Fat Liquors. *Werkm. Zeitg.* through *Ledertechn. Rundschau*, 1911, 77-8.—On the introduction of chrome tanning, it was found impossible to apply fat to the flesh in the old way for it went through the leather and issued through the grain, hindering a finish. The difficulty was overcome by the use of emulsions of fat with water, the so-called fat-liquors. These are applied, not locally to the surface, but in mass by the drum. Ready made fat-liquors are in the market, the principal constituents being soap, olive oil, neatsfoot oil, degras, glycerine, castor oil, etc. Castor oil soap is the best, prepared by stirring 10-12 l. castor oil at 30-35° C. into a solution of 1 kg. caustic soda in 4-5 l. water. A good recipe for a fat liquor is 5 kg. glycerine, 3 kg. castor oil in 100 l. hot water emulsified by gradual addition of 6 kg. castor oil soap dissolved in 50 l. water. For very fine leather, a mixture of solely 50 parts castor oil soap and 75 parts castor oil is used. Olive or neatsfoot oil can also be used. W. J. K.

The Valuation of Gelatin by Determination of the Melting-Point of Jellies. JULIUS HEROLD, JR. *Chemiker-Zeitung* [34] 203.—Ordinarily, this method is crude and the results unreliable. The author's improvement consists in immersing the bulb of a thermometer reading to 1/10 degree in the gelatin solution contained in a narrow test-tube. After this has set, the whole is suspended in warm water and the temperature recorded when the test-tube falls. A 1 mm. surrounding layer of jelly gives the best results. The water-bath should be near the melting-point, 1.5-2° higher. It was found that the melting-point increased with age of the jelly, but became constant after 1 hour. For any given gelatin, the melting-point was found to rise with the percentage present, being directly proportional; plotted graphically, a straight line resulted. With low grade gelatin, the change is least, *i.e.*, the line is nearer horizontal. W. J. K.

Gelatin Analysis. JULIUS HEROLD, JR. *Chemiker-Zeitung*, 35, 93-4.—On treating gelatin solutions with alkalies, the gelatinizing power is lowered, the loss being increased by heat. The glutin, which determines the gelatinizing power, is decomposed into glutose which is the adhesive component of glue. The determination of glutin and glutose are de-

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sirable therefore to value gelatin and glue. Chemical methods fail, for both substances give the same reactions with tannin, picric acid, etc. A precipitation of glutin by alcohol throws down glutose as well. The author has devised a method which employs the determination of melting-points of jellies described above. High grade gelatin was converted into glutose by heating with ammonia water under pressure and the dried product mixed in varying ratios with the original material. Twenty per cent. jellies from these had melting-points progressing from 32.6° to 31.3° C. for mixtures of 0 to 66 per cent. glutose; the glutose lowering the melting-point. The absolute melting-point cannot be taken directly as a measure, since it is greatly affected by impurities, for example, salt. The ratio of increase with the concentration is used, this being most rapid with pure gelatine. Hard emulsion gelatine (Höchst factory) was taken as standard, it analyzing 17.0 water, 1.0 ash, residue 82.0 glutin. The difference in melting-points for 20 and 10 per cent. jellies was 34.5 — 33.3 = 1.2° = a. For any other gelatine, $\frac{a}{1.2} = \frac{x}{82}$, x being the per cent. of glutin. In this way 68, 61, 41 and 13.5 per cent. glutin were found respectively in table gelatin, light clean bone gelatin, technical gelatin, low grade gelatin (already glue). An improved form of air-bath tube for the melting-point determination is described; it is supplied by Bender and Hobein, Karlsruhe i. B. The jellies are let stand ½ hour in a thermostat bath of 19-23° before transferring to the melting bath.

W. J. K.

PATENT.

Leather Dressing. U. S. Patent No. 994,446. THOS. A. DRAKE, Jersey City, N. J.

The material includes gum thus, lard oil, castor oil, menhaden oil, paraffin oil, beeswax and linseed oil, united by heat. Several combinations are mentioned, all including gum thus and menhaden oil.

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Journal of the

American Leather Chemists Association

Vol. VI AUGUST, 1911 No. 8

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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EDITORIAL.

The Committee Work of the American Leather Chemists' Association.

In a recent letter, the chairman of one of the most important of this year's committees states that he has written to each one

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of the members of the committee in regard to the work for the year but has received a reply from only one member. The chairman of another committee writes that of eight members only two replied when he wrote outlining the work of the committee. These examples are typical of the present attitude of the members of the A. L. C. A. towards committee work. It would seem that very shortly we must decide whether or not we wish to discard the committee method of carrying on the work of our association and if we do discard it we must decide on some new method of carrying on this work.

The early efforts of our association as a body were directed almost entirely to working out and perfecting methods of tannin analysis. The committee method of doing this work proved eminently successful. The advantages were obvious. In testing a new method or a modification of an old one the effect of the location of the laboratory and the personal equation of the worker are most important. A method which gave uniform results from many different chemists in many locations was pretty sure to be a satisfactory one and worth submitting to the association as a whole. Now that the methods of analysis, with some few exceptions, are fairly well established, the scope of committee work has had to be enlarged and the factors making it desirable have changed. Already we are beginning to attack some of the great problems of the leather industry. Is the system going to break down just when this most important and interesting work is approached? Are ionization, the acidity of liquors, the sulphite cellulose problem, tannery waste and other problems of this sort not suitable for committee treatment and are we going to leave the remaining problems in analytical methods in their present unsolved condition?

We must remember that there are few of us in this country so favorably placed in regard to individual research as are many of our colleagues on the other side of the water. It will be many years before we can hope for an environment which will produce a Procter or a Stiasny. In the mean time what we accomplish for the advancement of the scientific side of the leather industry in general must be done by working extra time and in addition to the routine work which has, perhaps, more immediate but no more important bearing on the good of our em-

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ployers. This time is at best, limited. Perhaps the trouble may be there is no time left over these days. But how can we better accomplish anything in the research line with what little time we have than under the committee system? Is it not the only way in which the little mites that each of us can spare can be added up into a respectable sized sum of research work?

Our JOURNAL has been a source of pride to us since the beginning of our organization, but if we look back over its five completed volumes we will not find many original articles by our own members. We do not have the time to write them. Are we going to have more time in the future? How well our committee work shows up in these volumes and how small the volumes would be without it! Even abroad, where so many have considerable time to devote to research and publication, it seems to be pretty difficult to get material for their journals and one is likely to read the same article in *Collegium, Der Gerber, Le Cuir* and *Leather*. If our Association drops the committee work is our JOURNAL not likely to become a mere reprint of what is published abroad with very occasionally an original article by one of our own members?

But need we or can we drop committee work? The committees as organized this year are broad enough in scope to interest each of us in at least one of them. We were allowed to choose the committees we wished to serve on. And we have accomplished almost nothing. It is not too late to accomplish something now. There are still several months before the annual meeting. If we are not in touch with the chairmen of our committees let us find out what they are doing and what they want us to do, then let us buckle down and do it. Under present conditions in this country it is only by carrying on the committee work to-day as vigorously and efficiently as it was carried on at the start of our organization that we can hope to make our Association continue as a success, and that we ourselves can be of maximum benefit to our employers and to the leather trade in general.

J. H. Russell.

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SOME ADVANTAGES OF THE GRAPHIC METHOD OF RECORDING RESULTS IN ROUTINE ANALYSIS.

By J. H. Russell.

The results of the analysis of a single set of tan liquors is likely to be misleading. Even where analyses are made frequently, the slight variations due to lack of uniformity in sampling and liquor running and unevenness of absorption of the tannin by the hide may easily direct the attention away from the real condition and tendency of the yard. These slight variations also make it difficult to study and, eventually, to correct, the seasonal changes in composition of a yard otherwise running on an even basis. If, however, the results of routine analyses are plotted as curves, vertically on the per cent. composition basis and horizontally by dates of sampling, the above mentioned variations sink into their place of relative unimportance and the true history and tendency of the yard is revealed. Ordinarily it is not necessary to plot all the results of analysis. Curves showing the tannin, non-tannins and acid of each of the new and sapped liquors of the tannage are usually sufficient to show the condition and tendency of the yard. The method is subject to indefinite expansion, for, by the use of various colored pencils and lines of different character, one can show any number of factors in the yard composition. In curves plotted for an ideal yard in which the liquors had just the desired composition and were keeping it, the lines would all be straight, horizontal and parallel. This condition can scarcely be even approximated in actual practice, but in general, the simpler the curves, the better the condition of the yard and the more uniform the resulting stock. The simple curves of a good yard are more a matter of pride to those responsible for them than of interest to those seeing them. It is when a yard is going through a time of stress, or the policy in running it is being definitely changed that the curves became not only interesting, but exciting. In Fig. 1 is shown a set of curves for tannin, non-tannin and acid from routine analyses of head and tail handler liquors over a period of six months. Analyses were made every two weeks. During the period shown, a decided change in the character of the liquors was made. At the beginning of the period they were on a high

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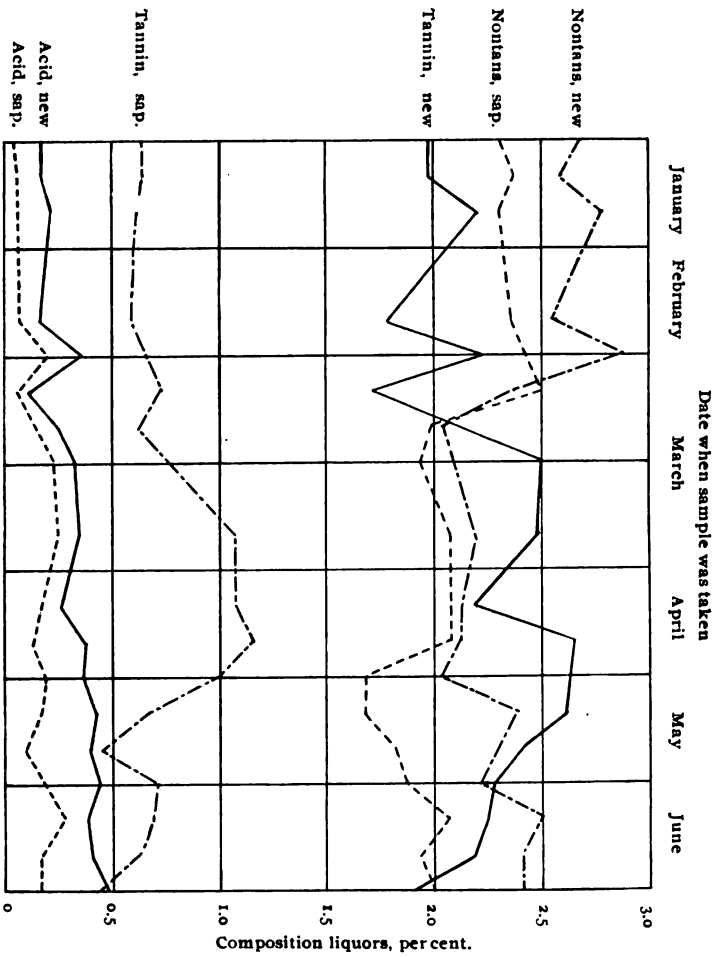
non-tannin basis which was later shifted to high tannin and lower non-tannin and finally to a basis lower in tannin, but somewhat higher in purity than at the beginning of the period. As

Fig. 1.—Graphic representation of analytical results on head and tail handlers over a period of six months.



good an idea can be gained of these changes by a glance at the curves as by a considerable study of the tabulated analytical results.

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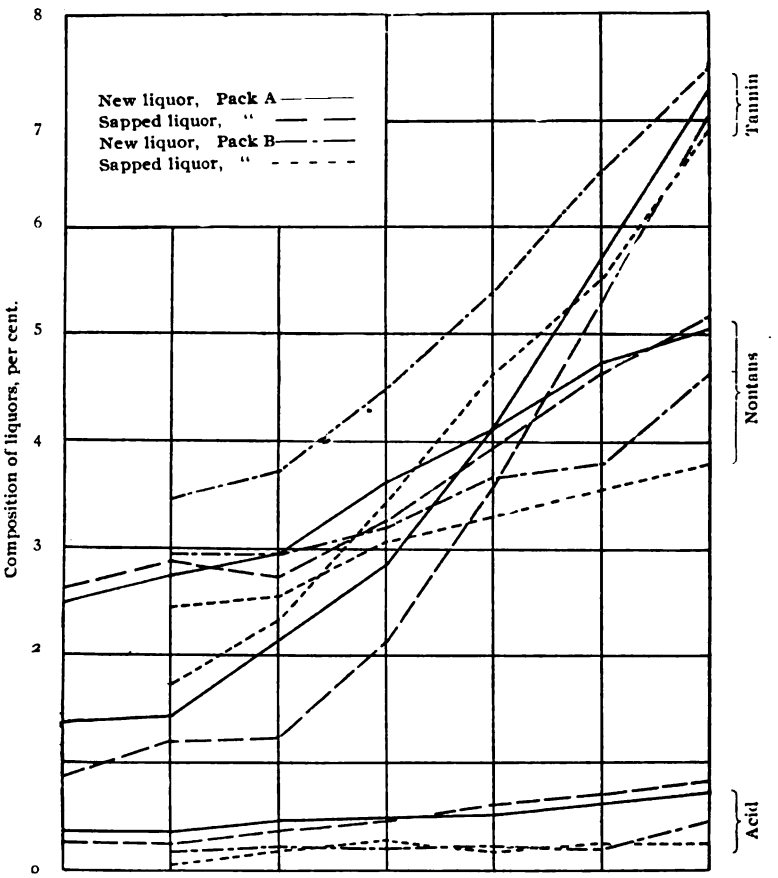
Another method of plotting results of analysis is used in following the tanning of test packs. The percentage composition, in this case, is plotted vertically and the stage in the tannage,

Fig. 2.—Graphic representation of analytical results on liquors from two test packs, A and B, from different tannages, showing history from handlers to the end of the last layer.



horizontally. With new and sapped liquor results plotted in this way one gets a good idea of the progress of the tannage, the sappage, acidity development, etc. Fig. 2 shows a compari-

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son of new and sapped liquors from two test packs tanned under quite different conditions. Of course, all these curves are interesting and valuable mainly as checked up by the results on the finished leather. Sometimes these results are sufficiently definite so that a section can be marked off on the curve and a note made stating just what effect that particular make up of the liquors had on the leather.

The chemist of to-day who is located at a tannery naturally wishes to enlarge his field of usefulness. The ordinary routine work can, under careful supervision, be turned over, largely, to assistants without special training along chemical lines. The chemist who would do this, must, however, be able to show definitely, first, that the routine work can be done accurately under his supervision, and secondly that the time he gains by turning the routine work over to assistants, he can use in a manner profitable to his employer. Research work is the most obvious field for the employment of this time and should certainly not be neglected. On the other hand, the value of the results of research work is problematical and the employer is justified in expecting something of definite and immediate benefit. Probably there is no field outside of the laboratory in which the chemist can more quickly make himself felt than that of tanning costs. He is peculiarly fitted to enter this field, for the figuring of tanning cost is largely an analytical matter. At the same time working in this field brings him in the closest touch with tannery problems and conditions. The link between the laboratory and the cost field is the cost of the unit of tan which involves the cost, strength and proportion of all the tanning materials used. For the strength of the materials the chemist must be depended upon and he must also correct the analytical tannin to what he considers the available tannin of the material. The results of his work can very well be shown by curves giving the proportion of tannin from each of the materials used in the whole amount of tannin and the cost of the unit of tan. Such curves are plotted with two vertical scales. One shows the per cent. of tannin each material furnishes in the total tannage for a given period. The other shows in cents the cost of a pound of tannin in the mixed tannage. Horizontally the curve is plotted in periods of time over which the proportions of the tannage and

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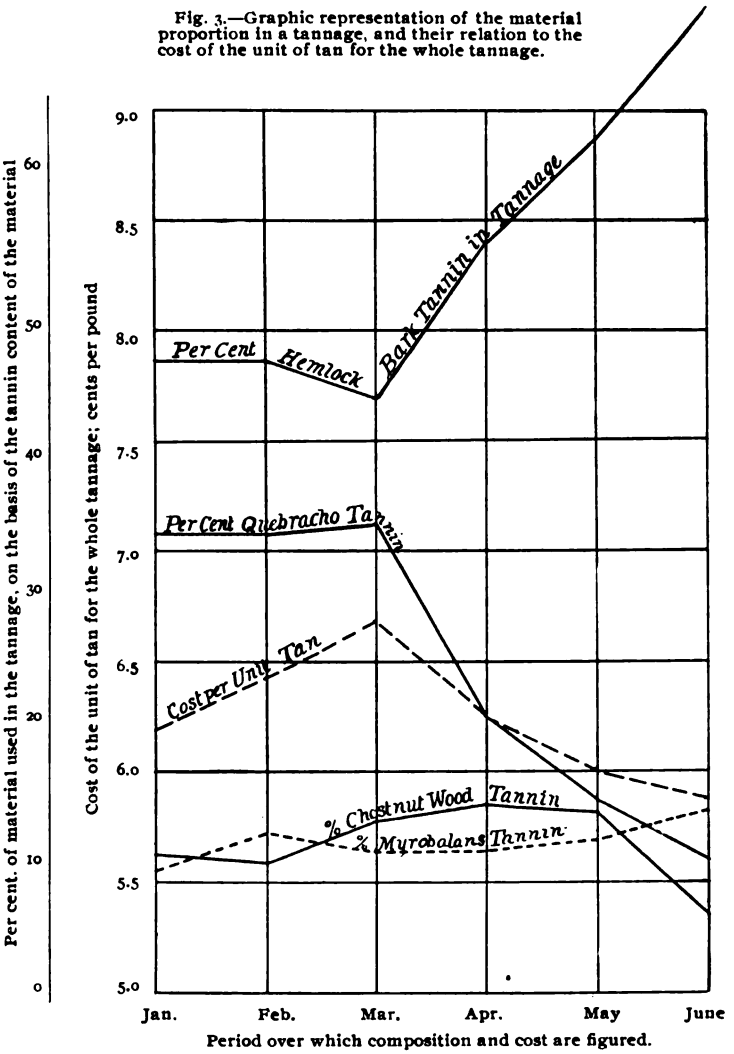
the cost of the unit of tan are figured. In Fig. 3 we have a set of curves of this order. Here again, instead of a diagram covering periods where the tannage has been on an even basis

Fig. 3.—Graphic representation of the material proportion in a tannage, and their relation to the cost of the unit of tan for the whole tannage.



as to composition and cost of the unit of tan, I have taken, rather, a section covering six months during which time a radical change was made in the proportion of tanning materials re-

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sulting in a corresponding change in the cost of the tan unit. Such results may easily prove misleading and can be intelligently interpreted only in connection with the figures for the total amount of tannin used with reference to the pounds of leather produced and taking into consideration also the yield and nature of the resulting leather. By putting notes or references as to these matters on the diagram where changes have been made, the danger of the curves proving misleading is avoided.

The graphic method may also be a considerable factor in the personal influence of the chemist on men in other departments. The average leach house man may not be much interested in figures of the periodical analyses of spent tans, but once he realizes the import of a curve for tannin in spent tan on a diagram and that the lower he can force the curve down the better he is doing his work, he takes pride in keeping his curve as low as possible. The yard man may not be interested in the actual tannin and non-tannin figures but when he realizes that a diagram of results on yard liquors which shows nearly straight horizontal lines usually means that he is doing his work well, he is likely to take more care in so making up and running his liquors that the analysis lines will always keep straight. The superintendent or owner of the tannery may not have the time or inclination to study and compare the results of analyses. He is more likely to give a few minutes study to a set of diagrams such as Fig. 2 which will show him how his yard stands to-day and how conditions compare with those of as long ago as the diagram was started.

This is a rather elaborate exposition of a perfectly simple and well known method, but so far as the writer's experience goes, there are few of the leather chemists who use the graphic method to represent their analytical results. The method is, of course capable of much wider application than is shown by the few examples given. It is hoped that these notes may be of benefit in calling the attention of those chemists who are so fortunate as to be located at a tannery, to the usefulness and convenience of the graphic method.

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NOTE ON THE CALORIFIC POWER OF SOME TANNING MATERIALS.

By A. W. Hoppenstedt.

Considering the difference in the composition of the tannins and the tanning materials, together with the question occasionally arising regarding the leaching of spent bark relative to its calorific-power, it seemed of interest to the author to make some calorimetric measurements of the principal tanning materials.

Clarified Quebracho Extract (Bisulphited), Ordinary Quebracho Extract, Chestnut Extract, Hemlock Extract and Oak Extract were selected. These were carefully dried, powdered, dried again and the determinations made on the resulting absolutely dry material. For the measurements, the Emerson standard oxygen bomb calorimeter was used. The following table shows the results obtained, together with the values of some substances of interest:

	Calories	B. t. u.
Clarified quebracho extract	5,265	9,477
Ordinary quebracho extract	5,710	10,278
Chestnut extract	4,248	7,646
Hemlock extract	4,895	8,811
Oak extract	4,952	8,914
Carbon	8,137	14,647
Cellulose	4,208	7,574
Starch	4,228	7,610
Cane-sugar	3,961	7,130

Accordingly, quebracho shows the greatest calorific power, followed by oak, hemlock and chestnut in the order named. It is interesting to note the higher values of the quebracho extracts. The difference in the results between the clarified quebracho extract and the ordinary quebracho extract is about proportional to the degree of bisulphiting. The high percentage of tannin and low percentage of non-tannins of these extracts would not account for the higher heat of combustion, so that it is evident that the percentage of carbon is largely responsible. This is further borne out by the low value given by the chestnut extract which is the only pyrogallol tannin represented. It will be of interest to note here the percentage of carbon in the purified tannins:

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	Per cent. carbon
Quebracho tannin	63.7
Oak tannin	59.8
Hemlock tannin	57.4
Chestnut tannin	52.1

It will be seen that the materials follow in the same order in calorific power.

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Buffalo, N. Y.

THE ECONOMIC POSSIBILITIES OF THE MANGROVE SWAMPS OF THE PHILIPPINES.[1]

By Robert R. Williams.

Tanning materials are being imported into the United States in such rapidly increasing amounts that the importations now form a large percentage of the total quantity consumed. In 1900 the assessed value of such imports was about 1,600,000 dollars which in 1910 had grown to a sum exceeding 6,500,000 dollars. The increase has largely been due to the economical manufacture of extracts and to the development of quick tanning processes which demand materials of high concentration. In 1909, the last year for which reliable figures are available, 10,779,177 dollars were paid for tanning extracts, while the total amount expended by American tanners for vegetable tanning materials was 21,904,927 dollars. By far the most important extracts are South American quebracho and domestic chestnut. The cost of the former in 1909 was 5,877,989 dollars, and of the latter, 3,579,929 dollars. Hemlock, palmetto, and gambier, supplemented in recent years by myrobalans and mangrove, constitute the remainder of extracts used in tanning.

Tanners in Europe also are becoming more and more dependent upon imported materials. European importations include a larger proportion of raw barks and woods, due to a slower development of extract tannage on that continent.

The extended use of mangrove bark, and more particularly

[1] Philippine Journal of Science, Jan, 1911. Continuation of the work begun by R. F. Bacon and Vicente Q. Gana of the Bureau of Science, Manila. *See this Journal*, March, 1911, p. 124.

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mangrove extract, is of comparatively recent development. The East African swamps have for a number of years furnished bark, chiefly for the German market. Twelve thousand two hundred and sixty-three tons, to the value of 250,409 dollars, found their way to American ports in 1909. The swamps of the Malayan region also have been a considerable source of supply. These barks, although of the same species as the East African, contain only 25 to 30 per cent. of tannin as compared with 35 to 40 per cent. in the latter. For this reason, exports have been limited to the manufactured extract known as cutch. A number of companies have successfully been operating in Borneo, Java, and Sumatra for several years. American tanners bought 700 tons of this extract in 1909, at a cost of 43,566 dollars. This article entered the United States duty free until March, 1906, (Treasury Decision No. 27,197) when it was declared dutiable. This caused a general decrease in production and closed one Borneo factory. Under the Payne tariff of 1909 cutch is dutiable at seven-eighths of a cent per pound.

The advantage which the Philippines enjoys in this respect promises to give opportunity for a profitable cutch industry in the Archipelago. All the species of mangroves of any importance in the Eastern tropics are found in the Philippines. The area of the swamps, though small compared with those of Borneo, Sumatra, and the Malay Peninsula, is considerable. The Bureau of Forestry estimates the total virgin swamps of the Philippines at 511,784 acres, which includes an area of 61,750 acres of well-developed swamps in Sibuguey Bay, Mindanao, a 24,700 acre tract in Mindoro, and a fairly compact area of good swamp in Palawan; but on other islands than the three mentioned the swamps are so scattered as to render profitable cutch manufacture very doubtful. The swamps of Tayabas and the Sulu Archipelago should perhaps be excepted.

"In Mindoro, Palawan, and Mindanao, the *Rhizophoraceae* reach as large size as anywhere in their range. *Sonneratia* also seems to reach its maximum development in Mindanao."

Only a few carefully estimated figures are to be found upon the tannin content of mangrove barks. Analyses made near the source of supply have not to any great extent been published. Apparently, samples analyzed elsewhere frequently have lost

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much of their tannin before reaching the chemist. Busse reports analyses of some East African barks and gives for comparison those of barks from the same region made by the "Deutsche Gerberschule zu Freiberg."

	Tannin (per cent.) Berlin (Busse)	Freiberg
Bruguiera gymnorrhiza Lam.	51.64	24.60
Ceriops candolleana Arn.	42.27	27.50
Xylocarpus granatum or X. obovatus	40.49	8.70
Rhizophora mucronata Lam.	47.99	21.30

He attributes the low results of the Freiberg school to improper packing for shipment.

Two analyses of *Rhizophora mucronata* Lam. from Zanzibar show 34.3 and 35.8 per cent. of tannin in barks containing 16.2 and 16.4 per cent. moisture, respectively. Blockey reports some analyses of Indian mangrove bark as follows:

	Tannin (per cent.)
Bruguiera gymnorrhiza	9.7
Kandelia rheedii	17.3
Rhizophora mucronata	4.5 6.1
Ceriops candolleana	18.0

Various trade notes give the barks of India as averaging 25 to 29 per cent. of tannin, which doubtless is more nearly correct. The results of the Freiberg school and those of Blockey certainly do not represent the average barks of the two regions.

The Philippine Bureau of Forestry has furnished the following report upon four samples of Philippine barks submitted to the Bureau of Plant Industry at Washington.

	Total solids	Soluble solids	"Reds"	Non-tannin	Tannin
No. 15335 B. F. (*Ceriops tagal* (Perr.))	58.58	49.02	9.56	13.19	35.83
No. 15336 B. F. (*Rhizophora conjugata* L.)	53.91	51.03	2.88	11.64	39.39
No. 15337 B. F. (*Bruguiera eriopetala* W. & A.)	37.36	36.81	0.55	10.15	26.66
No. 15338 B. F. (*Bruguiera parviflora* W. & A.)	24.43	19.82	4.61	7.27	12.55

EXPERIMENTAL.

The swamp area of the east coast of Sibuguey Bay, Mindanao, from the mouth of the Vitali River to that of the Bulaan, a

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distance of some 40 miles, has been taken as representative in a general way of the better swamps of the Philippines. Different species predominate in different areas and there are of course considerable variations in the stands of timber. However, in the matter of the tannin content of the bark of any given species, no considerable variation is to be expected in Philippine swamps of approximately equal development.

I have found that this area will yield about 8.8 tons per acre of fresh bark of mature trees of selected species averaging about 28 to 30 per cent. of tannin on the dry weight. Only four species are included in this estimate, all others being negligible from a commercial standpoint. The natural resources are sufficient for a profitable industry, the swamps being fully as valuable, acre for acre as many now being worked in the East Indies.

It has further been observed that, in general, the tannin content of the bark increases with the size of the tree. It is probable that the age rather than the size of the tree is the true coefficient of the tannin content, but since these trees show no seasonal rings of growth it is almost impossible more than roughly to approximate the age. Such variations from the general rule as will be observed in the tables given below, where the approximate diameters are noted, are easily accounted for by differences in the conditions of growth of the individual trees. However, further work must be done to establish the fact.

Like many other barks, these deteriorate when allowed to dry slowly in the air. Molds may grow on the fresh bark and rapidly destroy the tannin. Exposure to the air and light in any case causes oxidation, resulting in loss of tannin and production of red coloring matter. All samples, the analyses of which are given below, were dried over quick lime and placed in dark, air-tight bottles until analyzed. The analyses in all cases were made within sixty days after collection. Samples collected near Manila, dried and preserved in this manner, at the end of two months showed no losses of tannin exceeding 0.5 per cent. The analyses were made by the method of the Association of Official Agricultural Chemists, substantially as published in Bulletin No. 107 of the United State Bureau of Chemistry. Somewhat larger

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quantities of hide powder than those recommended were found necessary completely to detannize the solutions.

Data, both analytical and general, regarding the principal trees of the swamps are given below. Botanical descriptions have not been included.

Rhizophora Mucronata Lam. BACAUAN (Tagalog).

This tree is found in stands of even development, usually on

TABLE 1.—ANALYSES OF BARK OF RHIZOPHORA MUCRONATA LAM.[1]

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
1	9.2	60.4	39.6	15.7	23.9
9	9.2	60.8	39.2	13.7	25.5
10[2]	5.2	68.5	31.5	15.7	15.8
11[2]	6.0	75.7	24.3	12.0	12.3
18	8.0	67.6	32.4	11.1	21.3
28	12.0	65.0	35.0	14.6	20.4
45	12.8	59.1	40.9	14.7	26.2
60	10.0	58.6	41.4	12.5	28.9
63	8.8	58.0	42.0	11.4	30.6
64	9.2	54.3	45.7	11.9	33.8
65	10.0	56.2	43.8	14.9	28.9
66	12.0	60 0	40.0	13.0	27.0
69	12.0	61.2	38.8	12.4	26.4
72	18.0	56.6	43.4	12.9	30.5
73	8.0	63.9	36.1	15.3	20.8
80	8 to 10	57.0	43.0	12.7	30.3
81		55.2	44.8	15.0	29.8
82		56.4	43 6	11.2	32.4
83		56.4	43.6	11.8	31.8
84		55.1	44.9	15.8	29.1
85		61.8	38.2	11.8	26.4
86		61.0	39.0	12.7	26.3
87		58.5	41.5	13.3	28.2
Average	....	59.2	40.8	13.2	27.6

[1] An average tree will yield bark to the value of 4.97 pesos, at 0.286 peso per kilogram. One ton of fresh bark is worth 35.50 pesos. The peso Philippine currency is equal to fifty cents United States currency; 0.286 peso per kilogram equals 0.065 dollar, per pound.

These figures do not represent the value of the bark as such, but of the total tannin present at the current price of tannin extracts. (Letter of A. Klipstein & Co., New York, July 22, 1910). They are given for the purpose of comparing the various barks.

[2] Excluded from average as undersized tree.

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the water side of the swamp. It makes up two-fifths to one-half of the total timber producing commercially valuable bark. Its maximum diameter is 20 inches; the average 10 to 12 inches, excluding young trees below 8 inches in diameter. It attains a height of 50 to 80 feet. Three average-sized trees were found to yield 308 pounds each of fresh bark. The bark bears a thin, hard, outer scale easily removed from the inner bark, which is orange colored, non-fibrous and somewhat pulpy, and contains 50 to 60 per cent. of moisture. The wood is hard and heavy (specific gravity about 1.1 when dry), and is reddish in color. It is an excellent firewood and well adapted for structural uses in wet places. Analyses show 4 to 6 per cent. tannin. The leaves assay about the same.

A composite of the above samples gave 2.8 per cent. "difficultly soluble" tannins or "reds."

Rhizophora conjugata Linn. BACAUAN (Tagalog).

This tree in every way is similar to the preceding, but is much less common, amounting perhaps to one-tenth of the bark-producing timber. The bark is somewhat lighter in color when fresh than that of *Rhizophora mucronata,* while the woods of the two species are practicably indistinguishable.

TABLE 2.—ANALYSES OF BARK OF RHIZOPHORA CONJUGATA LINN.[1]

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
15	10.8	62.8	37.2	10.3	26.9
16	12.8	58.0	42.0	9.6	32.4
43	10.8	63.0	37.0	10.7	26.3
51	8.8	55.3	44.7	16.3	28.4
52	12.8	56.2	43.8	17.3	26.5
53	12.0	58.8	41.2	15.4	25.8
54	12.0	54.1	45.9	14.8	31.1
55	10.0	60.7	39.3	12.5	26.8
61	10.0	59.9	40.1	13.4	26.7
Average	10.08	58.8	41.2	13.4	27.8

A composite of the nine samples shows 1.9 per cent. of "reds."

[1] An average tree will yield bark to the value of 5 pesos. One ton of fresh bark is worth 35.77 pesos. See footnote "[1]" to Table 1.

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Bruguiera gymnorrhiza Lam. and **B. eriopetala** W. & A.

Both these species are known by the native name *pototan* or *pitutan*. They can be distinguished only by their flowers, the most obvious difference being in their color. Those of *Bruguiera gymnorrhiza* Lam. are red; of *Bruguiera eriopetala* yellow. When the samples were taken, in most cases flowers were not visible and the two species therefore have been taken together. They constitute about 20 to 30 per cent. of the workable trees. The maximum diameter is 40 inches; the average diameter 16 to 18 inches, excluding trees under 8 inches. Three average-sized trees yielded 418 lbs. each of fresh bark. The scale is dark, about one-fourth inch thick, and adheres rather strongly to the inner bark. The latter is of a dark orange-color, somewhat fibrous, and contains 40 to 50 per cent. moisture. The wood is like that of the other *Rhizophoraceae,* but is more valuable because of the size of the trees. It contains 6 to 8 per cent. of tannin.

TABLE 3.—ANALYSES OF BRUGUIERA GYMNORRHIZA LAM. AND B. ERIOPETALA W. & A.[1]

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
22	20.0	63.0	37.0	8.5	28.5
23	24.0	51.2	48.8	9.8	39.0
29	24.0	51.6	48.4	11.0	37.4
32	14.0	58.4	41.6	13.9	27.7
33	24.0	50.3	49.7	11.8	39.9
37	30.0	51.5	48.5	11.9	36.6
40	12.0	70.7	29.3	7.2	22.1
42	14.8	60.9	39.1	9.7	29.4
46	12.0	63.8	36.2	9.0	27.2
49	14.8	55.8	44.2	12.2	32.0
58	20.0	64.8	35.2	7.0	28.2
67	28.0	46.5	53.5	11.8	41.7
75	16.0	53.4	45.6	12.3	33.3
Average	19.5	57.2	42.8	10.4	32.4

A composite of above samples showed 0.3 per cent. "reds."

[1] An average tree will yield bark to the value of 9.70 pesos. One ton of fresh bark is worth 51 pesos. See footnote "[1]" in Table 1.

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Bruguiera parviflora W. & A.

The common name is *lañgaray* or *hagalay*. It is a tall, slender tree growing in very even stands and very plentifully. Its maximum diameter is about one foot, the average diameter 8 to 9 inches. An average-sized tree yielded 220 lbs. of fresh bark of dark red color, very fibrous in structure, and containing 35 to 40 per cent. of moisture. The wood is lighter in color and weight than *bacauan* and *pototan* and somewhat softer. It contains 1 to 2 per cent. of tannin.

TABLE 4.—ANALYSES OF BARK OF BRUGUIERA PARVIFLORA W. & A.[1]

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material: Insoluble	Total extract	Non-tannin	Tannin
6	8.0	81.4	18.6	8.0	10.6
12	8.8	87.2	12.8	5.6	7.2
20	10.0	86.5	13.5	6.1	7.4
21	10.0	85.1	14.9	6.8	8.1
30	10.0	84.4	15.6	7.0	8.6
31	14.0	82.8	17.2	8.8	8.4
38	10.0	78.3	21.7	8.6	13.1
41	12.0	85.4	14.6	5.9	8.7
59	8.8	82.4	17.6	6.9	10.7
62	12.0	78.8	21.2	8.8	12.4
70	8.8	84.3	15.7	7.3	8.7
71	8.0	85.7	14.3	7.7	6.6
74	12.0	81.6	18.4	10.0	8.4
76	10.0	85.7	14.3	6.6	7.7
Average	10.0	83.6	16.4	7.3	9.1

A composite of the above samples showed 5.6 per cent. of "reds."

Ceriops tagal (Perr.) C. B. Robinson. TAÑGAL (Tagalog).

Tañgal is now scarce in the Sibuguey Bay region. Its bark is highly prized by the natives for coloring rice and "tuba," and for dyeing. The wood is also of more value than any other mangrove. The charcoal supply of the Islands largely is made from it. Commercially, it is a negligible factor in this region.

[1] An average tree will yield bark to the value of 1.63 pesos. One ton of fresh bark is worth 16.30 pesos. See footnote "1" to Table 1.

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TABLE 5.—ANALYSES OF BARK OF CERIOPS TAGAL (PERR.) C. B. ROBINSON.

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
8	6.0	54.5	45.5	11.8	33.7
34	14.8	51.7	48.3	11.1	37.2
35	14.8	59.2	40.8	17.0	23.8
36	12.0	54.0	46.0	14.7	31.3
39	12.0	58.9	41.1	10.6	30.5
Average	10.0	55.7	44.3	13.0	31.3

Xylocarpus granatum Koen. PIAGAO (Tagalog).

This tree often reaches 20 inches in diameter, but it is not very plentiful. Its bark is exceedingly thin, usually one-fourth inch; it is dark on the exterior and bright red on the interior. A tree will not yield more than 44 to 55 pounds of bark. Its wood shows 6 to 8 per cent. of tannin. The wood is very beautifully grained and colored, and should be valuable for interior finishing.

TABLE 6.—ANALYSES OF BARK OF XYLOCARPUS GRANATUM KOEN.

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
7	8.0	62.8	37.2	12.2	25.0
57	18.0	70.0	30.0	9.1	20.9
Average	13.0	66.4	33.6	10.6	23.0

Xylocarpus obovatus A. Juss. TABIQUE or NIGUE (Tagalog).

In some of the higher parts of the swamps this tree occurs quite plentifully, attaining a diameter of 12 to 16 inches. Its bark, like that of the preceding, is very thin. Its wood is somewhat lighter in color and weight than *X. granatum*. The trees often are decayed at the heart.

TABLE 7.—ANALYSES OF BARK OF XYLOCARPUS OBOVATUS A. JUSS.

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material			
		Insoluble	Total extract	Non-tannin	Tannin
78	10.0	67.6	32.4	7.7	24.7
79	8.0	69.7	30.3	8.6	21.7
Average	9.0	68.7	31.3	8.1	23.2

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Sonneratia pagatpat Blanco. PAGATPAT (Tagalog).

These trees often grow in exposed places, and under such conditions are stunted and gnarled. Under more favorable surroundings they sometimes exceed 40 inches in diameter. The bark is dry and woody, sometimes containing only 15 to 20 per cent. of moisture in old trees. The wood is yellow-white but dark at the heart. It is moderately hard, suitable for general structural work.

TABLE 8.—ANALYSES OF BARK OF SONNERATIA PAGATPAT BLANCO.

Sample No.	Diameter of tree Inches	Parts per 100 of water-free material: Insoluble	Total extract	Non-tannin	Tannin
13	20.0	82.3	17.7	5.6	12.1
14	20.0	80.7	19.3	7.3	12.0
44	33.0	80.1	19.9	7.6	12.3
56	8.0	81.4	18.6	7.8	10.8
Average	20.0	81.1	18.9	7.1	11.8

A survey of the data shows that only four species can be depended upon to furnish a supply of bark. They are *Rhizophora mucronata, R. conjugata, Bruguiera gymnorrhiza* and *B. criopetala,* the two former commonly known as "bacauan," the two latter as "pototan" or "pitutan." Tañgal, which is the "teñgah" bark of Borneo upon which the manufacturers there depend to a considerable extent, is scarce on Sibuguey Bay. Both *Xylocarpus granatum* and *X. obovatus* yield too small quantities of bark tree to be remunerative. *Bruguiera parviflora* has a very low tannin content, as has *Sonneratia pagatpat.*

However, a use may be found for the last mentioned for blending with the more valuable barks, since it produces a leather of good, brown color, very different from any tanned by barks of the *Rhizophoraceae.* Some samples of leather were tanned with well-preserved barks by the method suggested by Parker and Procter,[1] using goat skin instead of sheep grain, as the latter was not obtainable in Manila.

No.	Tanning material	Description of leather
1	Bacauan	Dark red, somewhat thick grain.
2	Pototan	Not distinguishable from No. 1.
3	Pagatpat	Medium brown, porous, soft, smooth grain.
4	Bacauan.. / Pototan .. / Pagatpat . — equal parts	Reddish brown, better than either Nos. 1 or 2, grain smooth.

[1] Parker, J. G., and Procter, H. R. Numerical expression of color. *Journ. Soc. Chem. Ind.* (1895), 14, 125.

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In calculating the yield of bark in the area examined, only bacauan and pototan trees 8 inches or more in diameter have been counted. For this purpose seven rectangular areas of about one-half acre each were selected as representative after a fairly thorough exploration of the surounding swamp. These areas are distributed at approximately regular intervals between the mouths of the Vitali and Buluan Rivers. The yield of bark per tree was determined by felling three representative trees each of bacauan and pototan and stripping and weighing the bark. Bacauan averaged 310 pounds per tree, pototan 420 pounds. On this basis the area will yield about 8 tons of bacauan bark per acre and 2 tons of pototan. We may safely state the yield at 8 tons per acre of bark worth about 40 to 45[1] pesos per metric ton, at 0.286 peso per kilogram (6.5 cents per lb.) unit of tannin, allowing 50 per cent. for moisture.

The restrictions placed by the Bureau of Forestry upon the exploitation of the swamps will depend largely upon their condition at the outset. However, it is understood that in virgin swamps the cutting of trees over 8 inches in diameter will be permitted provided the wood is put to some commercial use. It is said that in Borneo and Queensland the standing trees are stripped as high as convenient and the tree left to die and go to waste. I am convinced that the bark can be gathered more economically by felling the tree and obtaining all the bark. A tax of 3 pesos per metric ton (about $1.40 per ton) is levied on the dry bark.

It is not my purpose to take up the question of the disposal of the wood. This problem certainly is the most serious one confronting the prospective exploiter of swamps distant from Manila. The market for mangrove woods for structural purposes at present is extremely limited. The firewood industry has been suggested as an outlet. Taxes were paid on about 200,000 cubic meters (about 50,000 cords) of firewood in 1909. However, most of this supply comes from swamps near the markets for which it is intended. It sells on an average all over the islands for about 25 pesos per 1,000 *rajas* (about 5 to 6 cubic meters) equivalent to about $8 per cord. After paying for

[1] This is not the market value of the bark as such. See footnote "1" to Table I.

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logging, sawing, splitting, and meeting transportation charges of at least 1.50 to 2 pesos per cubic meter and a tax of 1 peso there would be an exceedingly small profit even if present prices could be maintained.

If a market can not be found for the wood, destructive distillation might be resorted to, as there is every reason to believe that these woods are especially suitable for that purpose. The lack of a near market for large quantities of charcoal would of course be a great drawback. Aside from this, there can be no question but that such swamps can be exploited at a good profit.

Shipment of the raw bark might not prove profitable. Mangrove barks are quoted[1] at 18 dollars per ton in the United States. This is an extremely low price per unit of tannin, even in crude materials. It is probably due to the high coloring power of air-dried barks. It is possible that by kiln drying a better price might be obtained. However, Australia offers a much better market for such materials. The demand is steady and the better classes of tan barks bring as much as 7 pounds sterling per ton. Freight charges to Australia from the Philippines are also very much lower than they are to the United States. I estimate the cost per ton of dry bark, as follows:

	Dollars
Felling and stripping	4.00
Delivery at kilns	1.00
Drying	0.75
Tax	1.50
Freight (Australia)	6.25
Total	13.50

CUTCH MANUFACTURE.

Cutch is prepared by extracting the bark with water and evaporating the liquor to a suitable percentage of moisture. Cutch prepared by the best methods now in use has approximately the following composition and characteristics:

		Per cent.
Water		20
Tannin		50 to 55
"Insolubles"		2 to 5
Nontans	Ash	1 to 2
	Sugars	5 to 7
	Organic Acids, etc.	16 to 18

[1] Hide and Leather, Oct., 1910.

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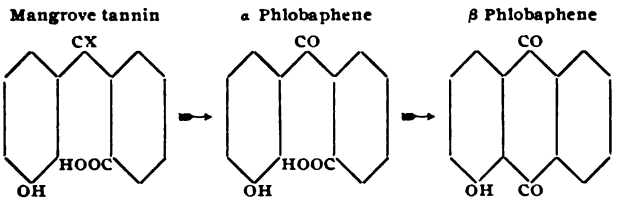
The extract produces a reddish brown leather, somewhat harsh and thick-grained, due to the high astringency of the tannin; but it gives a very satisfactory tannage when mixed with other materials.[1]

The tannin, coloring matter, "insolubles," and non-tans, each plays a part in the tanning process. Mangrove tannin is a "greening tannin" of the pyrocatechol series. Its empirical formula is generally accepted as $C_{24}H_{26}O_{12}$. Closely related to the tannin are the red coloring matter and the insolubles.



The more soluble, red colored substances is produced by oxidation, and this, by the splitting off of water, forms the less soluble phlobaphene which constitutes the bulk of the so-called "reds" which deposit as a slime upon cooling extract liquors. It is certain in any case that the tannin is the source of the red colored bodies. The soluble coloring matter, like the tannin, is absorbed by the hide to form true leather. The insolubles play a useful part in the latter stages of tanning by mechanically impregnating the surface of the hide and thus rendering it heavier and more impervious to water. More often than otherwise they are present in excess of the needed quantity and in that case are a nuisance to the tanner. If present in the more dilute liquors in which the hides are first immersed, they deposit in the pores or on the surface of the goods and prevent the proper diffusion of the soluble materials into the interior of the hide.

The rôle of the non-tans is quite a different one. Such glucosidal matters as are present ferment to form acids, chiefly lactic and acetic, which are necessary to keep the hide open and promote the diffusion of the tannin. If not present in sufficient amount, either acid or acid-forming material must be added. Pyrocatechol tannins are frequently deficient in this particular,

[1] *Collegium* (1902), 322-324; *Ibid.* (1904), 15-16. Also *Bull. Imp. Inst.*, London (1904), 2, 163-166.

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the non-tans being composed largely of salts. The[1] latter play no considerable part in tanning except that the presence of large quantities may be deleterious to the color and[2] grain.

Therefore, in the manufacture of an extract it is desirable to reduce the coloring matters, the "insolubles," and the metallic salts to a minimum and to obtain the maximum concentration with the minimum loss of tannin. The methods in use in Borneo are regarded as trade secrets by the manufacturers; however, they are known[3] in a general way, and the process presents no great difficulties.

Other things being equal, fine grinding promotes thorough extraction, especially if it be carried out at a low temperature; but for various reasons, fresh bark must be used and fine grinding of this material would be difficult. On this account I believe a preliminary kiln drying of the bark would be advisable, as it could be done cheaply and would make possible the use of much cheaper mills.

Extraction can best be done in wooden vats, using fresh water for the nearly exhausted barks and liquors of higher concentration for the less completely extracted material. With coarse bark the temperature would necessarily be high in order to break up the cells and give a thorough extraction. For finely ground material 50° to 60° C. is preferable. Parker and Procter[4] have shown that water at this temperature extracts more tannin and less coloring matter from most materials, and among them mangrove bark, than at higher temperatures. These comparisons were of infusions made by exhaustive extractions at various temperatures.

It was thought by me that most of the tannin might more readily be extracted at some other temperature. Experiments were made with *Rhizophora mucronata* and *Bruguiera eriopetala.*

Five grams of finely ground bark were treated two and one-half hours with 100 cubic centimeters of distilled water, the whole thrown on a sand filter and washed with 50 cubic centimeters of water at the temperature of extraction. The solutions

[1] Parker, *Journ. Soc. Chem. Ind.* (1900), 19, 313-315.

[2] *Jean, Rev. Chim. Ind.* (1896), 7, 269-271.

[3] *U. S. 60th Cong. House Doc.* 1505, 1, 221-228.

[4] Parker, J. G., and Procter, H. R., *Journ. Soc. Chem. Ind.* (1895), 14, 635.

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were made up to 250 cubic centimeters and analyzed. Color comparisons were made in Nessler cylinders with dilute solutions and calculated to a uniform tannin content.

TABLE 9.—EXTRACTION OF BARK OF RHIZOPHORA CONJUGATA LINN. AT VARIOUS TEMPERATURES.

No.	Temperature C°	Tannins extracted: Per cent. of maximum	Tannins extracted: Per cent. of total	Color, per cent. of maximum
1	30	89.0	74.1	70.0
2	60	100.0	83.0	75.0
3	80	88.8	73.8	90.0
4	Boiling	75.2	62.8	100.0

TABLE 10.—EXRACTION OF BRUGUIERA ERIOPETALA W. & A. AT VARIOUS TEMPERATURES.

No.	Temperature C°	Tannins extracted: Per cent. of maximum	Tannins extracted: Per cent. of total	Color, per cent. of maximum
1	30	95.5	72.1	97.0
2	60	96.6	73.0	97.0
3	80	96.1	72.7	98.0
4	Boiling	100.0	75.5	100.0

The results show that pototan (Table 10) is little affected by the temperature, while bacauan (Table 9) is best treated at 60°.

A large number of expedients were tried for clarification of the liquors. Moderately concentrated liquors upon cooling deposit a considerable part of the resinous "insoluble" substances within a few hours. Neither clay nor alumina increase the amount of "reds" precipitated nor hasten the subsidence. They do cause small losses of tannin. Animal charcoal is worthless. A dilute solution of albumen aids the clarification slightly, but causes some loss of tannin. Nothing as practical as simple cooling and subsidence has been found.

Suggestions and patent processes for dissolving the "reds" and bleaching tan liquors are very numerous. The problem presents many difficulties both because of the great ease with which tannins are precipitated or otherwise destroyed by very many chemical reagents and because of the intimate relation existing between the bodies which are to be separated.

Sulphurous acid was the first reagent tested by myself. Although of some value in treating certain extracts, it is worthless for that of mangrove. Neither at high nor low temperatures or pressures does it produce any brightening effect without the

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precipitation of large quantities of tannin. Carbon monoxide does not cause loss of tannin, but its bleaching effect is slight and not permanent. The method of Lepetit, very successfully used for "sulphiting" quebracho, destroys some tannin and neither bleaches nor clarifies. Sodium bisulphite was used in this test and the liquor was heated in an autoclave for eight hours at a temperature of 115° to 120° C. Alkaline salts and hydroxides, such as sodium sulphite, borax, ammonia, caustic soda and the like, dissolve the "insolubles" readily. As an alkaline liquor cannot be used for tanning, these reagents are useless. However it was found that treatment with a dilute alkali under pressure at 110° to 120° C. for three to six hours rendered the "reds" quite soluble in acid solution. Neither acetic, lactic, nor sulphurous acid precipitated them even after several hours' standing. Evaporation to dryness once more rendered them insoluble. It is particularly noteworthy that although the tannin of the treated extract was not destroyed by sulphurous acid, as was the case with the untreated material, there was no appreciable brightening of the liquor. Such an extract gives a nearly black leather and is unserviceable for tanning.

Nascent hydrogen is the best bleaching agent so far found. It is best generated with aluminum shavings and sulphuric acid, as the presence of small quantities of aluminum sulphate is not detrimental to the extract. The aluminum should be in excess so as to leave no acid to attack metal evaporating vessels. If the liquor is extremely dark and much acid must be added to bleach it, the bulk of the reagents in solution can be removed with baryta water. However, care should be taken that alkalinity is not reached, for the liquor will then darken more rapidly on evaporation and the leather is more likely to be stained by the barium hydroxide present.

By this method the "reds" are dissolved to a slight extent and the remainder coagulate and settle with the barium sulphate. An extract so treated gives a leather of good color, which darkens comparatively little on exposure to air.

Patents have recently been taken out for two processes especially designed for mangrove extract. One of them by Damkohler u. Schwindt (Eng. Pat. 24,899, Oct. 29, 1909),[1] is based

[1] Abstracted in *Journ. Soc. Chem. Ind.* (1910), **29**, 365.

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on the action of the "nascent hydroxides of metals" which are generated by electrolysis. A nonelectrolytic process included in the same patent is that of adding barium aluminate to the extract, and afterwards sulphuric acid or sulphates to clear the liquor. The complete specifications for the patent are not obtainable in Manila so that it was not thought worth while to test the electrolytic method. However, the nonelectrolytic process promises very well from the tests made with it. An extract so treated gave an excellent light-colored leather.

Another process designed by the Deutsche Versuchsanstalt für Lederindustrie u. H. Arnoldi (Ger. Pat. 220, 221, Sept., 1908)[1] is especially recommended for mangrove extract. It makes use of the action of aluminium amalgam. This process gave a more unsatisfactory result in my experiments than the one mentioned above. Leather produced from it was dark, although of smooth grain. No final conclusion can be reached until a fuller description of the process is obtained. With proper investigation one or more of the three methods last mentioned may confidently be expected to prove serviceable for commercial use.

TABLE II.—EFFECTS OF VARIOUS METHODS OF TREATMENT OF CUTCH.

	Water	Tannin	Non-tans	In-solubles	Total extract[2] Grams	Color of leather
Untreated extract.....	0.0	62.8	32.0	5.2	.....	Medium red
0.2 per cent. NaOH acidified with SO_2	0.0	53.3	40.1	6.4	104.0	Nearly black
Al + H_2SO_4.....	0.0	55.0	45.0	0.0	108.0	Yellowish brown
Barium aluminate	0.0	59.3	40.7	0.0	.....	Light reddish brown
Aluminium amalgam ..	0.0	58.6	41.4	0.0	.....	Medium red

Dialysis through a suitable membrane suggests itself as a means for diminishing the quantity of metallic salts present. Such a treatment is not essential to producing a good tanning material and would be of no great value except in giving a greater concentration of tans. Moreover, the process is an extremely slow one. Two thousand five hundred cubic centimeters of a 20 per cent. solution of extract were dialyzed for thirty hours with a continuous change of water over the diaphragm. The diaphragm was made by depositing a film of collodion on cheese-cloth. It

[1] Abstracted in *Chem. Abs. Amer. Chem. Soc.* (1910), **4**, 2588.

[2] This is the weight of extract obtained from 100 grams of the original material, calculated to the dry weight.

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had an area of about 100 square centimeters. At the end of the process only 12.85 per cent. of the mineral matter had been removed. The loss of tannin was very small.

The liquors properly treated, in as great a concentration as it is possible to obtain them in the process of extraction, should be evaporated *in vacuo* to a solid. Possibly, the earlier portion of the evaporation can be carried out by boiling in tall vessels with converging sides, such as will keep the liquor well protected from the air by a layer of water vapor. However, the last portions of the water must be removed by vacuum evaporation.

It is not possible to estimate the cost of the equipment for a plant with any accuracy from data now in our hands. The vacuum evaporators will make up the larger part of this expense. A suitable evaporator to handle 3 to 4 tons of solid extract per day of twenty-four hours would cost 35,000 to 40,000 pesos ($17,500 to $20,000). The other parts of the plant could be put up for an equal or less amount.

The cost of manufacture need not be great, as extremely cheap fuel and labor are available. Fresh bark should not cost more than 8 pesos per ton. On a basis of 50 per cent. moisture and a 90 per cent. extraction, 4.3 tons of this bark will produce 1 ton of cutch, worth 140 to 150 pesos ($70 to $75). It is believed that at present prices a net profit can be made of 50 to 60 pesos ($25 to $30) per ton. As there is a large demand for the product, its manufacture offers a promising field for investment.

Further data and suggestions as to manufacture can be furnished to prospective investors.

A SIMPLE VOLUMINOMETER FOR UNTANNED SKIN.[1]

By Joseph T. Wood and Douglas L. Law.

In Number 448 of the *Collegium* is an account by Mr. G. Grasser of an apparatus which he has devised for the measurement of the volume of samples of leather etc. In some experiments on the density of raw pelt which we were carrying out some time ago we made use of an apparatus on the same prin-

[1] *Collegium*, 1911, No. 465, p. 230.

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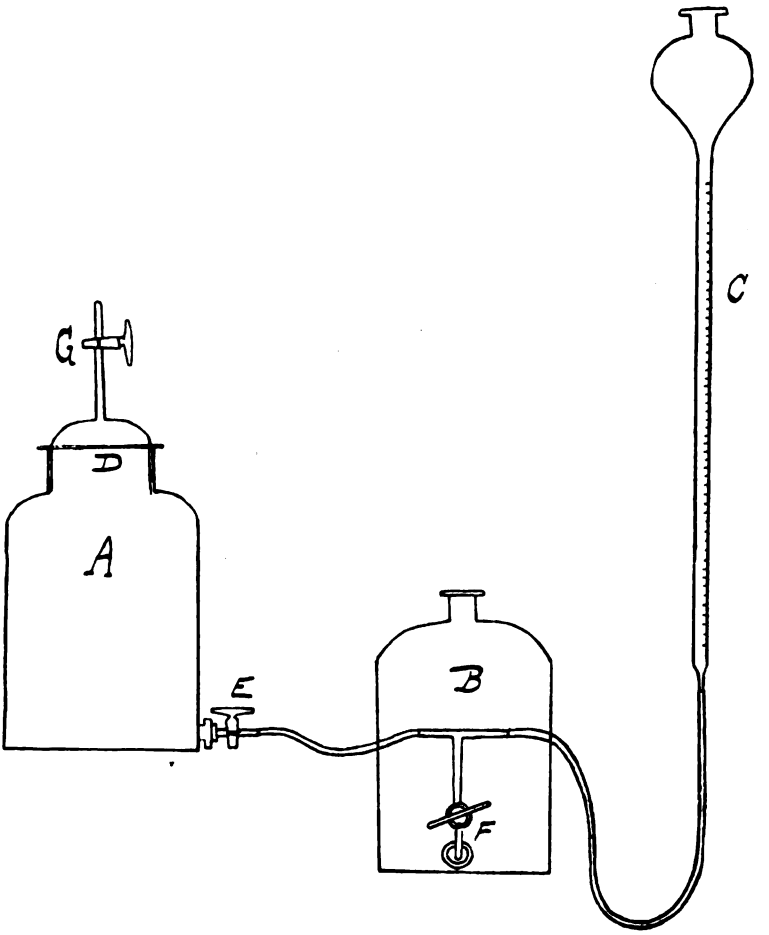
ciple and as it seems particularly applicable to the measurement of the volume of pieces of raw skin we have thought it of interest to describe it.

The apparatus consists of the two vessels A and B, connected



by means of thick rubber tubing to the burette C of which the top is enlarged to a bulb. The bottle A which was specially made for us by Messrs. Townson and Mercer, London, is of about 1 liter capacity and the wide mouth is closed by a stopper, accurately ground to fit the neck and extending down to the

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bottom of the neck. The upper part of the stopper is elongated to a tube which is closed by the tap G. The vessel A is also fitted with a tap E. The vessel B serves as a reservoir and is used to adjust the level of the liquid in the burette C by means of the tap at F. To find the volume of a piece of skin the method of procedure is as follows. The bottle A is filled with water up to the neck and the stopper D, carefully greased, is inserted. The tap E is then closed and the burette is filled with water. Then with the taps G and E open the bottle A is filled with water up to D by raising the burette. G and E are then closed and by opening the tap F the level of the water in the burette is adjusted to zero when F is again closed. G and E are then opened again and by lowering the burette the water in A is allowed to fall below the level of the neck of the bottle. E is then shut, the stopper D removed and the piece of skin is carefully introduced, avoiding air bubbles. The stopper D is then replaced with the tap open and by opening E and raising the burette the water is allowed to come up to the stopper D again. The taps G and E are then closed and the volume of the piece of skin read off directly from the burette scale. Volumes up to 50 cc. are measurable as described above, but larger volumes may be measured if a known volume of water is run from the burette into the reservoir before introducing the skin.

By using various solutions in the apparatus instead of pure water the real swelling or contracting effect of these upon the skin may be observed. The skin is introduced into the bottle A and the solution adjusted to G, which is then closed, then by leaving the tap E open the real swelling or contraction of the skin is measured by the rise or fall of the liquid in the burette.

ABSTRACTS.

The Use of Antipyrin in the Determination of Hübl's Iodine Number. F. Borde. *Pharm. Zentralbl.*, 1910, No. 27.—A solution of antipyrin is used to standardize the Hübl iodine solution, the end-point being a distinct yellow. The results are as accurate as with thiosulphate and starch and the method has some advantages. A solution of 1.88 grams antipyrin in 100 cc. of 50 per cent. alcohol is used; 1 cc. = 0.0254 grams iodine (Bougault). W. J. K.

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The Determination of the Saponification Number of Dark Oils. OTTO SCHUTTE. *Chem.-Ztg.* [34], 351.—5-15 grams oil are dissolved in 25 cc. pure benzol, 25 cc. alcoholic lye added and the whole boiled one hour, invert condenser, then titrated hot with ¼ N H_2SO_4, alkali blue indicator. When nearly neutral 30 cc. $CHCl_3$ are added to make the benzol layer sink. The color change from red to blue in the upper aqueous solution may be distinguished with practice in reflected light; a white background is of advantage. Pure dark blue, not violet, is taken as end-point. The blank test is made with the $CHCl_3$ present as this accelerates the color change about 0.2 cc. Good check analyses with known mixtures of mineral oil with rape seed oil and tallow are quoted.

W. J. K.

Apparatus for the Bromination of Fats. H. BULL AND L. SAETHER. *Chem.-Ztg.*, **34**, 649.—A revolving glass tube carrying a driving pulley serves to admit the bromine delivered from a burette and also as agitator. The lower end is bent in a spoon like form. The authors use this especially for hexabromide tests. 1 gram fat dissolved in 20 cc. glacial acetic acid—ether mixture, rinsing out with 5 cc. more. An average concordance within 0.09 per cent. was reached in 55 analyses.

W. J. K.

A New Apparatus for the Determination of Total Fats in Soap. A. RÖHRIG. *Zeit. angew. Chem.*, **23**, 2161-5.—The publication of "Einheitsmethoden z. Untersuchung von Fetten, Oelen, Seifen u Glycerin," Berlin, 1910, Springer, by the united soap manufacturers of Germany showed the need of unification in this analysis. Fendler and Frank (*Zeit. angew. Chem.*, **22**, 252) in their critical investigations conclude that only the absolute weights of the alkali salts give correct results for cocoanut and palm oil soaps while those by the official methods are false. As a matter of fact there exists no unified method suited to all cases. In the study of the usual wax cake and extraction method, little attention has been given to the inclusion of drops of water with the fatty acids as a source of error. This is especially liable with the Huggenberg's burette recommended by the convention. The author avoids this in his special apparatus (made by Hugershoff, Leipzig) which consists of an extraction flask surmounted by a graduated cylindrical neck or burette provided with a side cock. One to two grams soap (or more practically an aliquot part of a large charge in solution) are taken. For analysis of a fat, this is first saponified with ½ N. alcoholic KOH. The total amount of fatty acid to be finally weighed ought not exceed 0.5 gram. The soap solution in the flask is slightly acidulated with H_2SO_4, shaken and warmed. After cooling, 25 cc. of a mixture of equal parts ether and petrol. ether 35° b.p. are added to the 100 cc. mark or beyond, then 25 cc. more solvent and shaken. After settling and reading, one-half the ether solution is drawn off above, evaporated and the residue dried at 42-62°.

W. J. K.

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The Substitution of Bromine Numbers for Iodine in Fat Analysis. W. VAUBEL. *Zeit. angew. Chem.*, 23, 2078-80.—The iodine number is one of the most important constants, but its determination is often slow and the expensive reagents are unstable. The substitution of bromine numbers is desirable but not yet thoroughly worked out. Hazura probably first studied the bromine addition products of unsaturated fatty acids. Methods for the determination of the absorbed Br were proposed by Halphen 1889 (titrate excess with NaOH, eosin indicator), Levallois, Schlagdenhaufen and Fleury (thiosulphate). Hehner and Mitchell (Analyst, 1898, 13) developed the hexabromide method, precipitating by Br from a cooled solution of the oil in ether and glacial acetic acid. F. Telle (J. Pharm. Chim., 21, 117 [1905]) treated the fat in $CHCl_3$ soln. with excess of sod. hypobromite and KBr in acid soln. for 20 min., added excess As_2O_3 and titrated with hypochlorite to yellow. Oleic acid gave theoretic values. Stearic acid did not substitute.

The author considers his own method simpler. He employs either a solution of $KBrO_3$, 20 grams to the liter, adding KBr when used, or a bromate-bromide solution prepared from alkali and Br. Five grams fat are dissolved in 50-100 cc. $CHCl_3$, CCl_4 or benzin, placed in a stoppered liter flask. KBr added if needful, making up to 300-500 cc. H_2O solution. Ten cc. HCl, a fragment of KI and then an excess of $KBrO_3$ from the burette are added. After 1 min. shaking, the excess of Br is titrated back with sod. sulphite. As the end-point approaches, the yellow excess of Br disappears and the iodine appears. Thiosulphate gives irregular results and is not suitable. Drying oils require more solvent and bromate, with thorough shaking. It is easy to over titrate here where iodine is included in the precipitate, but the excess may be titrated back with bromate.

Analyses:

	Bromine number	Iodine number computed for Br	Iodine number
Cocoanut fat	5.1–5.2	8.1	8–9.5
Butter	22.3–22.3	35.4	36–38
Swine fat	30.0–33.0	47.6–52.2	50–70
Olive oil	53.1–54.7	84.2–86.7	79–88
Castor oil	54.8	86.8	83–86
Almond oil	61.6–61.6	97.7	93–97
Sesame oil	68.3	108.3	103–108
Peanut oil	57.6–57.6	91.3	83–100
Cod liver oil	79.8	125.5	.....
Wood oil	94.6	150.0	150–165
Linseed oil	107.7–107.7	170.7	171–201

W. J. K.

The Analysis and Chemistry of Fats for 1910. W. FAHRION. *Zeit. angew. Chem.*, 24, 241-54.—The following references are selected from this exhaustive review.

Literature.—Vol. III of Hefter's and Vol. III, part 1, of Ubbelohde's

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technical works (in German) have appeared. Heiduschka and Pfizenmaier have published "Beiträge zur Chemie und Analyse der Fette" and Seeligmann and Zieke, "Handbuch der Lack-u. Firmissindustrie."

Fat Extraction and Estimation.—E. v. Siebenrock (*Chem. Zentralbl.*, 1910, I, 1228) prefers ignited carnallite or $MgSO_4$ dehydrated at 250° to anhydrous Na_2SO_4 for drying ether. H. P. Pearson (J. Dyers and Color, **26**, 6-7) remarks that $ZnCl_2$ is soluble in ether and petrol. ether, likewise the chlorides of Al, Fe and Sn in ether, hence if present, should be first extracted with water. M. Riegel (Chem. Ztg. Rep., 1910, 356) separates fat and lecithin by boiling methyl alcohol.

Physical Constants.—A. Lissner (Chem. Ztg. [34], 657) determines the gravity of solid fats with adjustable water-alcohol mixtures. The mean between just floating and sinking is taken. The reviewer finds the method suited for limited samples of mineral oil. Carlinfanti and Levi-Malvano (*Chem. Zentralbl.*, 1910, I, 421) have accurately determined the melting points of mixtures of stearic, palmitic and oleic acids and employ these in combination with iodine numbers for quantitative analysis.

Glycerin.—For Hehner's method, M. Steinfels (*Seifensiederztg.*, **37**, 750) proposes to measure the excess of CrO_3 iodometrically. E. Divine (*Ibid*, 1068) recommends 45 m. heating on water-bath, 30 per cent. excess CrO_3, 25 Vol. per cent. H_2SO_4.

Total and Free Fatty Acids.—The reviewer finds the extraction flask of Hönig and Spitze, which should be better known, the best for rapid methods like that of Röhrig (above). O. Heller (Chem. Revue., **17**, 275) notes the variations in results according as ether or petrol. ether is used; oxy-acids are not dissolved in the latter. F. Marx (abstr. JOURNAL, **5**, 317) does not show that his benzol method for dark fats checks with the usual method on light colored fats. F. Mayer's method (abstr. JOURNAL, **5**, 318) is faulty because the large amount of water used will dissociate the soap. D. Holde (*Z. f. Elektrochem.*, **16**, 436) has shown that a neutral dilute alcoholic soap solution containing even over 40 per cent. alcohol yields a small amount of free fatty acid on benzin extraction. The use of gaseous HCl in Twitchell's method for separation of fatty acids from abietic acid is troublesome. H. Wolff (*Farben Ztg.*, **16**, 323) has found that with alcoholic H_2SO_4, the fatty acids may be esterified at ordinary temperature.

Unsaturated Acids.—C. Courtot (Chem. Zentralbl, 1910, I, 1847) finds in studying Hübl's original method, that in the iodine tincture the alcohol is gradually oxidized to aldehyde and acetic acid; equilibrium is reached in 7-8 months, about 20 per cent. of the iodine being reduced. W. Winkler (Seifensieder Ztg., **37**, 167) determines the bromine number of fats by shaking the CCl_4 solution with acidified bromate-bromide. (Cl. Vaubel, above). McIlhiney uses free Br in CCl_4 soln., avoiding immiscible solutions. Several investigators have found pure linseed oil to have iodine number as low as 160-164, although 170 was held formerly to be the lower limit.

Varnishes and Lacquers.—As substitute for the expensive linseed oil,

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hemp seed oil has been used with satisfaction. Soya oil is employed but the varnishes "creep" and are soft; 35 per cent. addition to linseed oil is the maximum advisable (another says 50 per cent.). It is difficult to identify and gives a low hexabromide number.

Soaps.—McBain and Taylor (Berl. Berichte., **43**, 321) from conductivity measurements conclude that normal soap solutions are not colloids while Botazzi and Victorow (*Seifensieder Ztg.*, **37**, 1170) hold the opposite view based on dialysis experiments. According to Donnan and Potts (Chem. Revue, **17**, 272) the emulsification of soap solutions by hydrocarbons depends upon a lowering of the surface tension of oil-water brought about by the soap; the effect increases with the molecular weight of the fatty acids. Von Hottenroth (Seifensieder Ztg., **37**, 601) determines free alkali by salting out the soap, precipitating the carbonate with $BaCl_2$ and titrating the filtrate; a blank test is necessary.

W. J. K.

Methods of Deliming. *Shoe and Leather Reporter,* June 15 and 22, 1911.—Pelt has the power of swelling in acids to an almost indefinite extent, at any rate, to such an extent that the internal cohesion of the substance vanishes and the pelt loses its organized structure.

The limed pelt when it enters the deliming liquor is in a swollen condition, the amount of swelling depending on the nature of the limes which have been given. In any case the first action which takes place is that the acid of the deliming liquor neutralizes the lime on the surface of the hide, and the resulting salt, (*e. g.* calcium lactate, if lactic acid be the delining agent) dissolves out into the surrounding liquor. If the action of the acid is allowed to proceed further than this surface action the whole of the lime may be so removed and the pelt is then in an acid condition. Parallel with this dissolving out of the lime and its replacement by acid, a change in the feel and appearance of the pelt will have taken place. At first the surface of the pelt will have "fallen" and will retain the impression of the finger nail but as the action proceeds the fallen pelt will begin to swell and plump up again due to the action of the acid.

The exact point at which the action of the acid is stopped, will depend on the class of leather to be made and also on the condition of the tan liquors as regards acidity.

Sulphuric acid may be used quite satisfactorily if great care is exercised, but an excess is to be avoided as excessive swelling would immediately follow besides spoiling the color.

Hydrochloric acid is not very suitable because of the effect of chloride in producing flat leather.

Sulphurous acid has been recommended by Procter because its acid properties are so weak that slight excess does little harm but the neutral calcium sulphite is insoluble and therefore to dissolve out the lime an excess must be used.

If water containing temporary hardness be used for deliming purposes,

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it is economical to soften the water by means of a cheap acid-like sulphuric or hydrochloric acid before adding the deliming acid, unless of course one is actually deliming with one of these acids. Otherwise some of the deliming acid will be used up in neutralizing the hardness of the water. As sulphuric is about three times as cheap as the ordinary deliming acids such as boracic, formic and lactic, it is more economical to soften the water first with sulphuric acid.

Of the other acids which are employed the most common are boracic, lactic, acetic, formic and more recently butyric acid.

Boracic or boric acid is one of the most popular and widely used of all the acids. It possesses several unique advantages over the others. In the first place, being a solid powder it is easy to handle and manipulate and the cost and trouble of carboys are avoided. The action of the acid on pelt is quite mild, with less swelling properties than some of the others, and it is not very soluble in water so that it is impossible to obtain very strong solutions of it and therefore if an excess were added it would be harmless. It neutralizes lime and forms calcium borate which dissolves out in the surrounding water. But above all, it owes its popularity to the beautiful smooth silky grain which it imparts to the pelt and which is maintained to the finished leather. Moreover it produces a bright color on the grain in the early tan liquors and has a marked tendency to prevent "drawn-grain" as well as permitting the use of stronger tan liquors in the early stages.

In using boric acid it is necessary that the hides should not touch one another and thus prevent the uniform action of the acid. If hides are left in contact in the deliming liquor for long, dark patches will appear at the points of contact, due to the non-action of the acid. This "kiss-mark" will produce stains when the hides come into tan liquor and may show in the finished leather as darker patches. The way to obviate this is either to suspend the hides so far apart that the grains do not touch or to give some sort of motion. The former plan is only applicable where large pits are available. Motion may be given by deliming in the paddle or by suspending on rockers, or more simply, by frequently handling the goods.

Lactic acid is now prepared by the fermentation of the residues from sugar manufacture. It possesses very strong plumping and swelling properties, being one of the best in this respect, so that excess must be avoided. It is one of the acids naturally found by fermentation in the tan liquors, this and acetic acid being the main constituents of the acidity of tan liquors so that it seems particularly suitable for increasing the acidity of the early tan liquors if they become deficient in acids. In cold weather when less fermentation takes place the amount of acid developed in the liquors is much less than in warm weather, and to obtain uniform results it is essential that the amount of acid and particularly the ratio of acid to tannin in the early liquors, should be kept as constant as possible. Lactic acid is especially applicable for covering any deficiency of acid in the tan liquors.

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Its action is the same as most of the acids, it neutralizes the lime, forming a soluble substance which dissolves out in the surrounding water and at the same time will cause the pelt to become plump and swollen.

As lactic acid is also one of the acids which are produced in the working of the bran drench it can be used as a substitute for drenching, although of course the effects are not in all cases identical, the mechanical cleansing and opening up of the fibers by the bran being missing, but the deliming and the "pulling-down" effects being very well effected, especially in warm weather when the danger of over drenching exists with the bran drench. When used as a substitute for the drench it works best at a temperature of blood heat, about 35° C. and motion in the paddle is to be recommended.

Formic acid until recently, could not compete with the other acid for use as a deliming agent, because its cost of production was too high, and the price of the finished article was much higher than that of the other common acids. Recently, however, it has come on to the market at a cheap rate and it is being very extensively used for almost all the purposes that the other acids may be used for, for deliming of both light and heavy skins, for pickling, for plumping in the early liquors and as a substitute for the drench.

Formic acid is a very strong acid and has a very energetic action on pelt. It comes on to the market as a colorless pungent smelling liquid, generally either as 60 per cent. or 75 per cent. strong. Weight for weight with the other acids it is one of the strongest acids there is, its molecular weight being very low, 46 compared with 90 for lactic acid, 62 for boracic acid, and 60 for acetic acid. These figures mean that the above quantities of the pure acids have equal powers in the neutralizing of lime. This is an important point to remember in the economy of the process and it will be observed that of the above acids, formic is the most economical. Since formic acid has such a strong action on pelt, it must not be used in excess. It is customary to add it in portions gradually, so that the grain and flesh are not too violently acted upon before the center is delimed at all. Otherwise the result will be harsh grain.

Acetic acid is usually prepared either from the crude pyroligneous acid obtained in the distillation of wood or as vinegar by the acetous fermentation of alcoholic liquids. In the destructive distillation of wood, an aqueous distillate is produced known as pyroligneous acid, containing acetic acid, methyl alcohol, acetone and resinous matters. This is purified by treatment with lime, but the purified product which generally contains about 50 per cent. of acetic acid still contains several impurities.

Pure acetic acid delimes very well, but the impurities in the commercial acid have always militated against its adoption as a popular deliming agent, there being a danger of producing an unpleasant harsh

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grain. If the acid could be obtained uniformly and sufficiently pure its use would probably be extended.

Butyric acid has only recently come on to the market in a sufficiently cheap form to enable it to compete with the other acids, but it is now prepared by a process which brings it within the tanners' means. It is claimed for it that it is cheaper than the other acids, that it does not dissolve hide substance and that it gives to the leather an odor which is characteristic of oak bark tanned leather. For deliming heavy hides there are two methods of proceeding, A., by suspension; B., by agitation.

A., by suspension. The quantity recommended is six to eight lbs. of the 80 per cent. acid per 1,000 lbs. of pelt. The deliming may be carried out in one or more pits. If one pit is used the operation lasts one day and the whole of the acid is added at once. If the deliming is conducted in two pits the operation lasts two days and half the amount of acid is added to each pit and the hides moved from one pit to the other on the second day. If three days are taken, three pits are used and the acid divided between the pits.

B. The deliming may be carried on in the drum, the quantity of acid required is the same as above but it should be added in installments rather than all at once. The liquors may be used for more than one operation. The best method is to suspend the hides first in the deliming liquor and then complete it in the drum, as this causes the deliming to take place slowly at first and thus the fibers are not worked too much.

With all the methods of using butyric acid it is recommended that the hides should be washed after deliming, either by drumming in water or by rinsing.

A very recent suggestion is the use of *ammonium butyrate*, especially for goods which enter the tan liquors in a neutral and fallen condition. It possesses the curious property of eliminating lime more quickly than free acids and it is claimed for it at the same time that the pelt becomes white in color and fallen. It may be used either alone or in conjunction with natural or artificial bates. It is suitable for box calf and heavy chrome leathers, and when used in conjunction with a bate, for glove leather. For use with pelt for box calf the quantity recommended is 1 lb. to 1½ lbs. of the ammonium butyrate to 100 lbs. of pelt, the butyrate being dissolved in 300 pints of water at 35° C. The pelt is introduced into this solution and paddled for half an hour, then allowed to rest for 2 hours and further paddled for half an hour. The end-point of the deliming is detected by touching a cut edge of the pelt with phenolphthalein solution. Where the lime remains unaltered a red coloration is produced and where the pelt has been delimed there is no such coloration (this is a simple test which can be used to detect how far deliming has taken place in any method). When the deliming is complete the pelt is rinsed in water at 35° C. for half an hour when it is ready to enter the tan liquors.

For chrome sheep the method of working is the same as above, but

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at least 1½ lbs. of ammonium butyrate should be used for 100 lbs. of pelt.

For chrome goat use 2 lbs. for 100 lbs. of pelt if no bate is to be given. If a bate or puer is also given it is recommended that the deliming be commenced in butyrate and finished in the bate, reducing the amount and length of time of the latter.

Alum Tannage in Small Tanneries. *Gerber Courier*, June 3, 1911.—The small tanner is often called on to "taw" a small lot of hides. This can be done well and profitably on a small scale. Proper liming is very important; should extend over 24 to 30 days. Wet-salted hides are best. If dry hides are used, they should before liming be well soaked, excess of flesh removed and again soaked in clean water. After unhairing, the hides should be soaked in warm water and then thoroughly cleaned by stoning and scraping.

Next the hides go to the bate, which should be prepared from ¼ sack of wheat bran that has been put to soak in hot water in a covered vessel three or four days before. The bating bath is at about 34° C. (93° F.). In this the hides remain, with motion or frequent handling for 12 to 14 hours in summer, or 1 to 2 days in winter. The hides must "fall" and become soft and pliable. When pressure on the grain with the finger tip leaves a depression, the bating is completed.

For the tannage of three or four hides 200-300 liters (50 to 75 gallons) of water at 15° C. (59° F.) suffice. Three kilos (6½ lbs.) of alum are dissolved in 6 to 10 liters (1½ to 2½ gallons) of water, and to this while boiling 1 kilo (2 1/5 lbs.) of salt is added. Half of this, well stirred, is put in at first, and after the tannage has continued 3 or 4 days, with frequent handling, the other half is added; the whole time being 10 to 12 days. If a small drum is available, the period may be much shortened. Half the alum solution is put in with 50 liters of water, and the hides drummed for two or three hours. The other half of the alum is now added and the drum run two hours. After this they are drummed a little while each two hours, and the tanning is complete in 10 to 12 hours. After drying in an airy place without direct sunlight, the hides are laid overnight in damp sawdust, best in a covered chest. Then follows softening on a scouring beam; then another drying and another scouring. Finally the flesh side is cleaned by rubbing with pumice-stone. L. B.

A Harmless Method of Disinfection for Hides Infected with Anthrax. PROF. A. SCHATTENFROH in *Gerber-Courier*, June, 17, 1911.—Hydrochloric acid and common salt are used, the hides lying for one to three days in a solution containing 1 per cent. acid and 10 per cent. salt. After this they may be shipped damp without further treatment. Since the presence of so large a proportion of salt hinders the ionization of the acid, it might be expected to diminish the disinfecting power. This was found not to be the case. The process may be varied considerably. Experiments with infected sheepskins and goatskins showed that while a solution containing 1 per cent. acid and 8 per cent. salt at 70° F. took

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one or two days to kill all the anthrax spores, a 2 per cent. acid and 10 per cent. salt solution at 104° F. took only six hours. This work was done in the Hygienic Institute of the Imperial University in Vienna. L. B.

PATENTS.

Treated Leather. U. S. Patent No. 997,513. CARL E. SCHMIDT, Detroit. Mich.

Evaporating and Concentrating Apparatus. U. S. Patent No. 995,776. JOSEPH E. DUNN, Philadelphia, Pa.

Leather-Working Machine. U. S. Patent No. 995,575. JAKOB SCHMIDT, Durlach, Germany.

Process for the Treatment of Chrome-Tanned Leather. U. S. Patent No. 996,080. ROBERT W. GRIFFITH, New York, N. Y.

The process involves the treatment of the leather while wet with lactic acid.

Staking Tool. U. S. Patents Nos. 996,053 and 996,054. GEORGE W. BOWERS, Somerville, Mass., assignor to Hammel, Riglander & Co., New York.

Tanning Process. U. S. Patent No. 996,509. OTTOKAR HENRY NOWAK, Chicago, assignor to Dermiforma Company.

The hides are treated with liquors containing whey which has undergone lactic fermentation.

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Journal of the

American Leather Chemists Association

Vol. VI SEPTEMBER, 1911 No. 9

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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EIGHTH ANNUAL CONVENTION.

The 8th annual convention of the A. L. C. A. will be held at Washington, D. C., December 7, 8 and 9, 1911.

H. C. REED, *Secretary.*

EDITORIAL.

Many of the articles published in scientific journals must be read by persons whose native language is different from that in which the articles are written. If all who write on scientific subjects would remember this fact, and try to write as clearly and simply as they can, it would save much time and vexation to their foreign readers. Much of the matter which is printed in continental languages presents to English-speaking readers difficulties which are quite unnecessary, being due to the writer using complex forms of expression where simpler ones would do at least as well. On the other hand, some of our scientific writers use English so obscure that some sentences are hard to understand even for those of us whose native language is English. A hundred years ago it was thought that learned treatises ought to be written in learned language. In all departments of science, except perhaps medicine, this view is going or has gone out of fashion. Let us not only avoid the intentional use of big words and long involved sentences, but also the careless use of language which may obscure our meaning and perplex our readers.

NOTES ON THE OFFICIAL METHODS OF THE A. L. C. A.

By J. H. Yocum and T. A. Faust.

The official methods of the A. L. C. A. have not been subjected to many alterations during the past four or five years, and although the present methods are the results of thorough collaborative work, yet there remain clauses which are rather vague, and admit of several interpretations, which may account for some of the discordances in the results obtained by different chemists in different laboratories.

We desire to call the Association's attention to some of these statements which appear to us vague in their meaning, or in which the original idea is misconstrued. Some of the differ-

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ences in results are caused, no doubt, by lack of observance of the details as laid down; this paper, however, bears principally upon the lack of preciseness in the methods themselves. The Association in a large measure owes its success in the past to the methods devised and authorized by it, and it is only after several years' experience with these methods, that the minor weak points crop out, which may be the cause of some of the slight differences in results among chemists at present.

Under Section 1. Crude Materials, Paragraph (1) Moisture Determination, the method reads, "Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis." Under Section IV., Paragraph (15), to which Paragraph (1) refers, the statement is made that the temperature should not be below 98° C. and the time shall be 16 hours.

These limitations of temperature at least are subject to criticism, in that with a low gas pressure and other conditions that exist in laboratories, there is no certainty that 98° C. can be maintained during the night. It would appear that some modification of the temperature to a lower degree, say 95° C., for this drying operation for the period specified in the Alsop oven, be considered. It hardly seems necessary on finely ground crude tanning materials to dry for the 16 hours specified, as it has been found that a shorter period of time at this temperature will effect the removal of the moisture. Some period ranging between 6 and 10 hours for this purpose, will no doubt effect the result desired.

Under Section 1. Paragraph (4) Extraction of Sample, no doubt the greatest differences in extractions are due to the different types of extractors used by different operators. The Teas extractor is the one most commonly used, and answers the requirements of removing at least one-half of the extractive solution from continued heating. The method calls for extraction until the gelatine salt solution fails to give a precipitate, but in the case of some rich tanning materials, an end point is not reached until 3, 4 or even 5 liters are extracted. We have found that by extracting 20 or 25 grams of fresh tanning materials (the richer tanning materials such as valonea, mangrove bark, myrobalans, divi divi, etc.), removing 1,000 cc. in 2 hours of the ex-

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tracted solution through an outside tube away from the influence of the sustained high temperature, and then refluxing for 15 hours, removing 1,000 cc. additional, that practically all the tannin, at least the active tannin, is removed. This is in line with the modifications suggested in the January number of the Journal.

Under Section 1. Paragraph (5) Analysis, we would call attention to the various methods of reporting analyses. This applies not only to crude materials, but to all other materials subject to a moisture determination, and reported both as "absolutely dry" and "air dry." It has been our habit to report first, the moisture; second, the analysis of the material on an absolutely dry basis; and finally, the tannin, calculated to the basis of the material's content of moisture as received at the laboratory.

It follows from this, that any change in moisture in samples from materials taken at the time the weights used for billing are obtained, may have a considerable influence on the value of the material paid for. In other words, the sample which is taken at the time that the weights are taken, should be carefully preserved, so that change in moisture content will be prevented. We have known cases where samples were drawn and remained in an office for some time, exposed to the atmospheric conditions existing in the office, where the moisture as found by the chemist had been reduced to such an extent as to entirely vitiate the value of the sample as an indication of the material's condition at the time it was weighed.

In this connection, it is likewise of considerable importance to know how to return spent materials, in that the materials rich in tannin, (valonea, myrobalans, etc.), during the process of leaching will lose at least half of their crude weights against the same moisture content of the spent material's weight. In the case of hemlock bark, with about 18.00 per cent. of total solids removed, about one-fourth of the original bark weight is lost.

The percentage of tannin found by analysis in spent materials, must be calculated back to the original fresh material. This correction depends upon the quantity of solids removed during the leaching operation, but for leach house control, a standard can be used for each individual tanning material. Moisture in the fresh material must also be taken into consideration. These

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facts call for a more uniform method of reporting spent materials.

Under Section II, Paragraph (6) Amount and Dilution for Analysis, the method reads, "Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottles. Such quantity shall be taken as will give from 0.35-0.45 grams of tannin per 100 cc. of solution. Dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C." This method is not precise enough to restrict the conditions that may exist in the laboratory. The method states that the temperature must not go below 20° C. during the period of time between its solution and the beginning of filtration, but it does not state at what temperature the solution should be kept over night, during this period of time. In the analysis of ordinary quebracho, or in fact any material containing a high percentage of insolubles, the temperature of the solution during the night has been found to influence very materially the amount of insolubles found in the extract.

We have carried on experiments keeping certain extracts between 28 and 30° during the night, and others between 20 and 21° during the night, and in every case the lower temperature showed a considerably higher percentage of insoluble matter, the method being carefully followed in the actual analysis. It would appear from this that the difficultly soluble reds, remaining in a warm medium during a considerable period of time, and then being suddenly subjected to the temperature outlined in the method (20° C.), do not come down in the same quantity, and are not evident in the analysis to the same extent as would be the case by chilling from 80° C. to 20° C. in a limited time, maintaining the temperature at approximately 20° during the period of time called for by this paragraph.

An extract which has been analyzed and dissolved in the summer months and cooled to 20°, will show a less quantity of insolubles than does the same extract when analyzed during the winter months and cooled to the same temperature, the variation being in the establishment of an equilibrium at the summer temperature of, say 28 or 30°, and an equilibrium at the winter temperature of, say 20 or 22° during the 12 to 20 hours.

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We have found with ordinary quebracho a difference of one-half to 1.00 per cent. in insolubles caused by this factor, which of course affects the tannin to the same percentage. For this reason, we would suggest that the council take cognizance of these facts, and limit the temperature during which precipitation of the insolubles occurs at least 6 hours before filtration for soluble solids, and that the limits be between 20 and 23° C.; and that the minimum and maximum temperature of the solution during filtration shall not exceed these limits.

In view of the difficulty of limiting temperature conditions during the period of cooling (12 to 20 hours), it might be advisable to change the present method so that it would more closely agree with the I. A. L. T. C. method which states, "Liquid extracts shall be weighed in a basin or beaker, and washed with water, well mixed and rapidly cooled to a temperature of 17.5° C., after which they shall be accurately made up to the mark, again well mixed, and filtrations at once proceeded with."

While we do not agree with the specified temperature of 17.5° C., it would not be inadvisable to cool to 20° C., after which the solution shall be made up to the mark and immediately filtered, which would obviate the variations in insolubles due to standing for a considerable time at different temperatures, as well as shorten the time required for the analysis.

It is essential that the manner of cooling by different chemists, be uniform, as well as that the method adopted shall enable each chemist to cool the solution uniformly. This will be best done by having a bath in which the temperature is kept at about 15° C. By frequently shaking the solution and noting the temperature from a thermometer inserted in the flask, the temperature of the solution can be absolutely regulated. This bath should be in use also during the period of time in which the soluble solids are being filtered.

This same difficulty arises in the filtration of soluble solids. When the solution is brought to 20° C. at the time of collection of soluble solids, the temperature of the laboratory will influence the percentage of insolubles, in that if the laboratory is warm, the solution will rise in temperature.

In 1903, Mr. Small brought up this question at the St. Louis meeting, and while a minimum limit was adopted as suggested

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by Mr. Small, no maximum limit was, although he suggested the maximum of 25° C.

In the filtration of soluble solids, the official method calls for the use of 75 cc. of the solution and 1 gram of kaolin in the preparation of the filter-paper, and after pouring the solution from the filter-paper, to refill the paper and collect filtrate for evaporating as soon as the filtrate comes clear. However, 75 cc. is not sufficient to fill the paper, and if the method is then followed out and the paper filled after the original solution has been poured off, the top part of the filter-paper which has not had its affinity for tannin satisfied, will absorb tannin from the solution being filtered for collection. We would like to suggest that the filter-paper be filled instead of using a definite quantity which is insufficient. This would overcome the objection to the present reading of the method.

In reference to non-tannins, it seems that there is too great a latitude in the percentage of water that the hide-powder may contain at the time of detannization. We find that the non-tannins made with a hide powder containing 70.00 per cent. of moisture, and those made with a hide powder containing 75.00 per cent. of moisture, will not agree as closely as they should, and that the latter will generally show a higher non-tannin figure than the former. However, Mr. Hoppenstedt finds the reverse of this, that the non-tannins are lower when the hide powder contains 75.00 per cent. of moisture than when the hide powder contains 70.00 per cent. of moisture. It would appear that an investigation of this question is warranted, and if variations in the non-tannins are due to the percentage of water in the hide powder, then the limits should be changed from what they now read (70.00 to 75.00 per cent.) to some more precise method of procedure.

It is an undisputed fact that in the majority of cases the differences in tannin results obtained by chemists on tanning materials, are due to the sample itself. This is shown by the procedure adopted by numerous chestnut extract manufacturers of having sealed sworn samples taken at the time a car is loaded, one sample being analyzed for the extract manufacturer, the other for the purchaser. Often tanners, not being members of the A. L. C. A. and not acquainted with the methods of procedure to be

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followed in the proper drawing of samples, do not draw a fair average sample. Even the chemists themselves frequently place different interpretations on the reading of the rules for sampling.

The method for the sampling of solid extracts does not offer as much opportunity for differing samples as do crude materials, especially mangrove bark. The rules laid down for the sampling of crude tanning materials are vague, and it is difficult or impossible to follow them at the majority of places where samples are drawn.

More difficulty is experienced in the proper sampling of mangrove bark than in probably any other tanning material. Where a 10,000 bag shipment of mangrove bark is to be sampled, the rules specify that 1.00 per cent. (100 bags) be emptied in uniform horizontal layers, at least 5 equal samples taken from top to bottom through the pile at uniformly distributed spots. Now, in most places where samples are drawn, it is impracticable to empty 100 bags of mangrove bark and follow these rules, and it therefore becomes necessary to cut the bags and take a sample according to the personal judgment of the sampler. In consideration of the fact that samples from different bags of mangrove bark of the same shipment may vary as much as 10.00 per cent. in tannin, it is absolutely necessary that good full samples be drawn from each one of the 100 bags sampled, that the entire sample be rough ground, properly quartered, this ground again and properly quartered, and the sample for analysis taken therefrom. This will yield a fair average sample.

Many chemists do not take the precaution to rough grind the whole sample, and consequently introduce an error in the drawing of the sample to be analyzed.

In cases where two chemists are drawing samples, one representing the buyer and the other the seller, the best policy is for the chemists to rough grind the whole sample, mix together, quarter down, and each chemist take his sample from opposite quarters, thus obviating any difference in the sample itself. The same applies to a lesser extent to the sampling of myrobalans, sumac, divi divi, etc., but there is not the wide variation in these materials that there is in mangrove bark.

In the case of valonea, owing to the fact that the beard contains more tannin than does the cup itself, also that this beard is

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so very fragile and easily broken into fine particles, sampling of valonea, unless consideration be taken of the bottom of the bag, is extremely difficult.

Probably the better way is to empty the bags as called for in the method, not more than 10 in a pile, being careful to see that the beard does not run through the pile by agitation, and then to immediately draw the sample from the pile.

Solid extracts which lose their moisture very readily are required to be wrapped in paraffine paper, but after the sample has stood for several weeks, especially in hot weather, traces of moisture may be seen on the sides of the bottle. Mr. Norris has found that by using a bottle with no shoulder, and making the bulk of the sample so as to fit snugly into the bottle, the above objection was overcome.

In reference to the extraction of leather with 95.00 per cent. alcohol, the advantage of the method proposed by Mr. Geo. Riker was the fact that the constant dissociation of the leather under sustained high temperature during the extraction with water, is obviated by the use of alcohol. Anyone who has extracted a number of samples of leather with water at the official temperature of 50° C., knows that the leather coagulates into a soggy mass, and that the combined tannin seems to be continually acted upon by the solvent, removing it, and that no definite end point for tannin is reached, whereas in the extraction with alcohol, this objection is not encountered, and the combined tannin is not affected to the same extent by alcohol as by water.

The solubility of sugars and glucosides complicates the alcoholic extraction to almost the same degree as the water extraction, but the solubility of epsom salts in alcohol is so slight that in ordinary cases this can be ignored. The alcohol method therefore possesses two distinct advantages over the water extraction, namely the extraction of the actual uncombined tannin without interference or dissociation of combined tannin, and the fact that sulphates can be left out of consideration, in ordinary analyses.

We would also call attention to the question of color tests. It is doubtful whether any two chemists in the entire Association make there color tests in identically the same manner. The broadcloth method does not appeal to the tanner, and does not give sufficient indication of the actual color of the tanning ma-

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terial on hide, to be of any value, and should be acted upon in its provisional aspects by the council, so that it would not further cumber the methods.

It appears, however, that if the same quality lamb skins be used (obtained from a central source, as is the hide powder at present), and if the same percentage of tannin in solution be used, each chemist to follow identically the same procedure, which should be outlined as a method by the Association, the question of color tests could be put upon a uniform basis. In that tanners and extract manufacturers require color tests, it must follow that the chemist shall produce them, and such variations as now exist in these color tests, are certainly out of the question.

Several excellent methods of making color tests have been suggested, and a Committee could determine the most suitable one, and that particular method should be adopted by the Association.

THE EMPLOYMENT OF THE ELECTROMETRIC METHOD FOR THE ESTIMATION OF THE ACIDITY OF TAN LIQUORS.[1]

PART II.

By J. T. Wood, H. J. S. Sand, and D. J. Law.

In part I,[2] of this paper (J. S. C. I., 1911, **30**, 3) a brief description of the electrometric method was given as employed by us for the estimation of the acidity of tan liquors. Several details, regarding particularly the form of hydrogen electrode most suitable for our purpose, were at that time left open. We have now had the opportunity to examine these matters, as well as to consider thoroughly other practical points in the application of the method.

In Part I the special advantages of the electrometric method for the determination of hydrion concentrations were pointed out, and the probable importance of such concentration, particularly in the swelling of hide, was referred to. As the last named matter had, however, been already previously indicated by Procter and Seymour-Jones in their exhaustive paper on the methods

[1] J. S. C. I., July 31, 1911.

[2] Journal A. L. C. A., March, 1911.

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hitherto in use for the determination of the acidity of tan liquors (J. S. C. I., 1910, **29**, 1454), and is, we understand, being further pursued by them at the present time, we do not propose to enter into this matter beyond giving a few analyses of tan liquors.

With regard to the hydrogen electrode, we hoped to be able to recommend a form in which platinum or iridium was burnt on to a surface of glass, and subsequently coated electrolytically with platinum black according to the proposals of Luther-Brislee (Z. Physik. Chem., 1903, **45**, 222). We have found, however, that the tendency of the metal coating to flake off the glass during the process of platinizing is so great as to render the electrode unsuitable for practical purposes. Even when the platinizing current was only a few milliamperes per square cm. the platinum coating has been known to flake off completely. We have also compared a stationary form of hydrogen electrode at present on the market (Köhler) for purposes of titration, in which the liquid is stirred only by the escaping hydrogen bubbles, with the forms we have hitherto used in which the liquid is stirred by hand by the hydrogen electrode itself, the latter being suspended by a cord at a distance of a few millimeters above the bottom of the beaker. As the result of this comparison we have found that the latter form is more convenient and rapid to work with. In Fig. 1 we show an electrode which we have designed with a view more especially to combine rigidity with rapidity of saturation, and ease of manipulation. The electrode was made for us by Universitätsmechaniker Fritz Köhler, Leipzig, and embodies the results of experiments on the most suitable size of platinum plate. The latter are in agreement with those of Salm (Z. Physik. Chem., 1907, **57**, 471).

The platinum plate consists of a piece of very thin foil which is wrapped round a cylindrical body of glass, A, and is held to the latter by some platinum wire, which passes through the glass and up the stem, E, where it is continued in the copper wire, B, the platinum wire, C, and finally in the terminal, D, fitted in the manner described by one of us in connection with the auxiliary electrode (Sand, Trans. Faraday Soc., 1909, **5**, 159). The stem, E, is fused in the manner depicted into a wider glass tube, F, which can be connected to the rubber supply tube, H, for the hydrogen. The tube, F, ends a short way above the platinum

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foil, and over it is slipped the tube, G, which is just wide enough to allow it to slide up and down F readily. A piece of thick walled soft rubber tubing, R, holds G firmly, and F sufficiently to keep G in position without hindering it from being pushed up and down when desired. During the operation of platinizing,

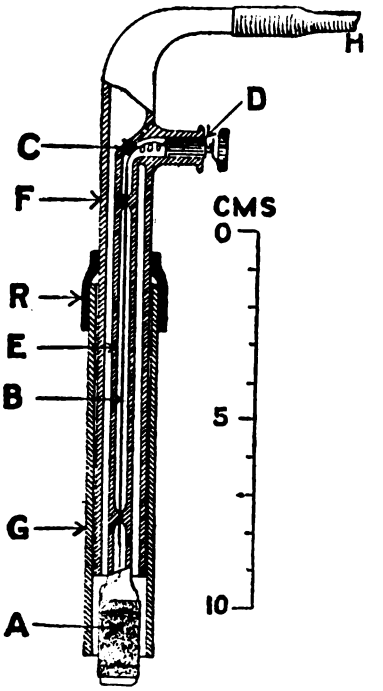

Fig. 1.

G is pushed up completely. While the electrode is in use G is adjusted to be a few mm. above the bottom of the foil, thus allowing the latter to dip into the liquid by this amount, whereas during the time the electrode is left filled with hydrogen when not in use, G is pulled down as far as possible, and at the same time the rubber delivery tube, H, is clipped as close to the electrode as possible. We have found that hydrogen may now be obtained commercially in cylinders of a degree of purity sufficient to allow it to be employed for the saturation of the hydrogen electrode without further purification (The Knowles Oxygen Co.,

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Wolverhampton). The electrode is made of fairly thick glass tubing to make it as little fragile as possible. It will be seen that its form causes the hydrogen to sweep past the platinum plate fairly rapidly, thus ensuring rapidity of saturation, and that the plate has at the same time a very considerable degree of rigidity. Its dimensions are, external diameter of the cylinder 11 mm., height 16 to 20 mm. As already mentioned, the electrode is suspended from a ring fixed to the burette stand by a piece of string, so as to be a few mm. above the bottom of the beaker. Attention may here be drawn particularly to the advantage which the hydrogen electrode offers for the titration of tan liquors in that the escaping gas hinders oxidation during neutralization. Thus a solution of gallotannic acid may be neutralized completely with N/10 alkali without any appreciable darkening when the hydrogen electrode is employed, whereas darkening always occurs at the neutral point during ordinary titration, oxidation also alters the amount of alkali used. It has already been pointed out by Sörensen (Comptes Rend., Laboratoire de Carlsberg, 1909, **8**, 59)[1] that large quantities of proteid matter in a liquid render all ordinary indicators unreliable, in contrast to which, the hydrogen electrode remains unaffected. Such proteid matter derived from the skins is always met with in tan liquors, the weaker the liquor, the greater being the proportion to tannin.

With regard to the other apparatus employed, there is little to add to what has already been stated in Part I. As will be pointed out later an accuracy of 1 centivolt is very considerably greater than anything that has ever been attempted hitherto with ordinary indicators, and it is, therefore, more important to arrange the method of working in such a manner that gross errors are unlikely to occur at any time, than to attempt to push the accuracy higher in any one direction.

The voltmeter attached to the potentiometer box gives readings to one-fifth centivolt, and if checked from time to time by reference to a standard cell is perfectly reliable. The instrument we have used has been in constant use for three years without any variation in its accuracy. Seeing that other sources of error, such as contact potential, between the liquids, are greater than

[1] Abstr. this Journal, April, 1911, p. 198.

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the error of reading the potentiometer, this is considerably quicker and more convenient than the method in which the slide wire is used. We adhere to our recommendation of the normal calomel electrode with 3.5 N potassium chloride as the connecting liquid. The reasons we have for avoiding a saturated ammonium nitrate solution as the connecting liquid have been stated by one of us (Faraday Soc. Trans., 1910, **6**, 18, Discussion). We protect the auxiliary electrode from light by wrapping it round with insulating tape. When not in use, the limb containing the 3.5 N potassium chloride solution should be kept empty in order to prevent the liquid from diffusing back into the main body of the electrode, and thus producing small errors. It should be pointed out here that any error produced in this way would, under similar circumstances, be very much greater with a decinormal than with a normal calomel electrode. In addition to this, the latter has the advantage that the conductivity of the connecting thread of liquid is greater, in consequence of which the zero instrument will respond more sharply, and any slightly faulty insulation will be less likely to cause serious error through leakage. It is advisable to keep a second standard electrode for reference, and to check the auxiliary electrode against it periodically, using normal potassium chloride solution as the connecting liquid. Another very useful check, not only on the auxiliary electrode, but also on the potentiometer box, consists in determining the hydrogen potential of normal sulphuric acid, normal potassium chloride being the connecting liquid. The value 0.328 volt should be found (Wilsmore, Z. Physik. Chem., 1900, **35**, 300).

In the first part of this paper the question regarding the voltage to be taken as the end point of the titration was left open pending the determination of a value which might be found to correspond to a hydrion concentration just producing a plumping effect on skins. In the meantime, we recommended the use of the value 0.69 volt corresponding to the hydrion concentration of pure water. As already explained, we have still left this question open, and therefore still adhere to our provisional recommendation. In the meantime, it may be found useful by many to have the formula by which the voltage observed with our apparatus corresponding to the exact point of neutralization

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of any weak monobasic acid, or in other words, by which the hydrogen voltage of solutions of its sodium or potassium salts may be calculated. The corresponding hydrion concentration, C, is given by the formula,

$$CH = \sqrt{\frac{k_w\, k_a}{c}}$$

(Salm and Friedenthal, Z. Elektrochem., 1907, **13**, 128) in which k_w is the dissociation constant of water, k_a that of the acid, and c the concentration of the salt (sodium or potassium) formed by neutralization and expressed in grm.-molecules per liter. Making $k_w = 1.2 \times 10^{-14}$ and substituting into formula (1) of Part I of our paper we find:—

$$\pi = 0.683 + 0.02875 \log \frac{c}{k_a}.$$

Thus taking for acetic acid $k_a = 1.8 \times 10^{-5}$, we find for a normal solution of sodium acetate $\pi = 0.82$ volt; for a decinormal solution $\pi = 0.79$. These numbers confirm the fact, probably not generally recognized in ordinary titration, that the alkalinity of a salt such as sodium acetate increases with the concentration. It must not be supposed that a determination performed on the solution of a commercially obtained sample of a pure salt will lead to the calculated hydrion concentration. It must be borne in mind that ordinarily prepared salts usually contain traces of occluded acid, which are sufficient to vitiate the results owing to the delicacy of the method. Thus the potential of N/10 sodium acetate (Kahlbaum) in ordinary distilled water was found to be 0.69 volt. In boiled out water it was 0.71 volt, and it only became equal to the calculated value 0.79 volt, after adding two drops of N/10 alkali to 25 cc. In his very thorough recently published study of the quantitative theory of indicators (J. Amer. Chem. Soc., 1910, **32**, 8158; *see* J. S. C. I., 1910, 1039) to which special attention is drawn, Noyes recommends (p. 839) that the ratio between the hydrion concentration corresponding to the correct neutralization of an acid, and that shown by the indicator employed in the titration, should if possible be kept within the limits 3.5 and 1/3.5. Translating this into terms of the electrometric method this would mean that an accuracy of ± 3.1 centivolts should be aimed at.

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A question that may frequently occur when an acid such as acetic is to be titrated in the presence of a much weaker one like carbonic or gallotannic, is the following: What is the potential and hydrion concentration when an amount of strong alkali has been run in just equivalent to the acetic acid originally present? Questions of this kind are by no means new, and are closely related to the theory of the "avidity" of acids. We indicate the original concentration of the first acid (acetic) by c_1, the original concentration of the second acid (carbonic or gallotannic) which is treated with sufficient accuracy as a monobasic acid, by c_2, and the concentration of the base added by b. Then it may be readily calculated, *e.g.*, from equations given in Abegg and Von Ende, Electrolytic Dissociation Theory (Wiley, 1907), p. 97, that the concentration, H, of the hydrogen ions is represented by the equation,

$$H^{\cdot 2} + \left(K_1 + K_2 - \frac{k_1c_1 + k_2c_2}{b}\right)H + K_1K_2\left(1 - \frac{c_1+c_2}{b}\right) = 0$$

in which K_1 and K_2 are the dissociation constants of the two acids respectively. For the case proposed above, the amount of base added is just equivalent to the amount of the first named acid present, we therefore have $b = c$, which by substitution to the equation given yields,

$$H^{\cdot 2} + K_2\left(1 - \frac{c_2}{c_1}\right)H - \frac{c_2}{c_1}K_1K_2 = 0.$$

This equation may be utilized to give an answer to questions like the following: When carbonic acid is present in a solution of sodium acetate what must be its molecular ratio to that of the sodium acetate in order that the solution may show the hydrion concentration of pure water? (10^{-7} grm.-mols. per liter corresponding to 0.69 volt). Substituting $H = 10^{-7}$, $K_1 = 1.8 \times 10^{-5}$ for acetic acid, $K_2 = 3 \times 10^{-7}$ for the first dissociation constant of carbonic acid, we find the value 0.7 per cent. for the ratio C_2/C_1. This means, for example, that N/10 solution of sodium acetate would have its hydrogen potential reduced from 0.79 to 0.69 volt by a carbonic acid concentration of 0.0007 gram-molecules per liter.

In the following table (I) we give hydrogen voltages determined for various pure acids occurring in tan liquors. The con-

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centration of these was found by titration with caustic soda, phenolphthalein being the indicator. Where possible, the voltage has also been determined by calculation, the hydrion concentration being derived with sufficient accuracy from the formula $C = \sqrt{Kc}$, in which K indicates the dissociation constant of the acid and c its concentration in gram-molecules per liter (vide *e.g.*, Abegg-von Ende p. 41). From this we find the hydrogen voltage by substitution into equation (1) (Part I) to be $\pi = 0.283 - 0.02875 \log Kc$.

TABLE I.

Acid	Concentration	Determined volts	Calculated volts	K
Acetic	N/10	0.445	0.448	1.8×10^{-5}
Formic	N/10	0.412	0.418	21.0×10^{-5}
Lactic	N/10	0.402	0.423	14.0×10^{-5}
Iso-butyric.....	N/10	0.450	0.451	1.4×10^{-5}
Normal-butyric	N/10	0.446	0.450	1.5×10^{-5}
Carbonic.....	Saturated	0.510	0.511 for N/25	3.0×10^{-7}
Gallotannic	1%	0.500	..	..

The differences between calculated and experimentally determined values do not exceed 1 centivolt in the majority of cases, and are probably due to contact potential at the junctions of the liquids. The hydrogen potential of an artificial tan liquor made up as follows was also determined: Acetic acid, 0.35 grm.; lactic acid, 0.25 grm.; tannin, 0.50 grm.; glucose, 1.00 grm.; water, 100 cc. The value 0.440 volt was found, and when the tannin and glucose were omitted the practically identical result 0.445 volt was obtained. On comparing these numbers with those given below for liquors actually taken from the tannery we observe very considerable differences, the actual tan liquors exhibiting hydrion concentrations which are between approximately one-fifth and one-hundredth of the hydrion concentration shown by the artificial liquor. The reason for this was found to lie in the presence of calcium and other salts which find their way into the liquors from the goods brought into them. We are probably not wrong in assuming that the plumping and other effects produced on the skin by the liquor will also be correspondingly diminished by these calcium salts, and that the older a tan liquor is, and the more lime salts have therefore been allowed to accumulate, the feebler will be its acidic action on the hides, and also, that a certain quantity of acid added to an old

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liquor containing large quantities of lime salts will produce less effect in plumping the goods than a corresponding amount added to a fresh liquor almost free from such salts.

In the following table (II) we give numbers which illustrate the effect produced on the hydrogen potential of various acids of decinormal strength by adding salts to them.

TABLE II.

Acid		Salt added		Hydrogen potential	
Name	Cc.	Name	Grams	Observed	Calculated
Acetic	..	..	..	0.445	0.448
Acetic	25	Sodium chloride	1.462	0.440	..
Acetic	25	Sodium acetate	2.050	0.586	0.590
Acetic	20	Calcium acetate	0.0158	0.498	..
Acetic	20	Calcium acetate	0.1580	0.552	..
Acetic	20	Calcium acetate	1.580	0.608	..
Butyric	..	..	..	0.446	0.450
Butyric	20	Calcium butyrate	0.0215	0.508	..
Butyric	20	Calcium butyrate	0.2150	0.560	..
Butyric	20	Calcium butyrate	2.150	0.612	..
Lactic	..	..	..	0.402	0.423
Lactic	20	Calcium lactate	0.0218	0.450	..
Lactic	20	Calcium lactate	0.218	0.498	..
Lactic	20	Calcium lactate	2.18	0.522	..
Formic	..	..	..	0.412	0.418
Formic	20	Calcium formate (dried in oven)	0.013	0.452	..
Formic	20	Calcium formate	0.130	0.498	..
Formic	20	Calcium formate	1.300	0.540	..

It will be seen from the table that the effect produced on the hydrion concentration of decinormal acetic acid by the addition of sodium chloride in normal strength is small, in fact the hydrion concentration is slightly increased. The addition, however, of sodium acetate crystals ($NaC_2H_3O_2 + 3H_2O$) in 0.604 normal strength reduces the hydrion concentration to about one two-hundred-and-fiftieth of its former value (by calculation from equation 1, Part I). The hydrion concentration, C, which was required in order to arrive at the calculated value of the potential from formula 1, Part I, was derived from the formula, $C \times A = Kc$, in which the acetic-ion concentration, A, was assumed to be about 0.4 normal, the sodium acetate being supposed to be dissociated approximately to 65 per cent. The concentration, C, of the undissociated acetic acid was taken as decinormal, and the value shown in Table I was given to the dissociation constant,

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K. The concentrations of the calcium salts taken approximate roughly to hundredth normal, decinormal, and normal respectively. It will be seen that increasing the concentration of the salt ten-fold raises the hydrogen potential by about five centivolts, and that the effect fully explains the potentials observed in the case of actual tan liquors.

A few words should here be said about the acidic effect of tannin. As may be seen from Table I, the hydrogen potential of a 1 per cent. solution of gallotannic acid (Kahlbaum) indicates a hydrion concentration greater than that met with in many tan liquors. The titration of this liquid with N/10 caustic potash, however, showed that only 1.8 cc. of alkali were required to bring the hydrion concentration of 20 cc. of the solution to that of pure water. The hydrion concentration of a freshly made quebracho extract solution showing 1 per cent. tannin (by the hide powder method) was $P_H^+ 4.53$.[1] It required the addition of 4.6 cc. N/10 caustic potash to 100 cc. of the solution to bring it to the neutral point 0.69 volts, $P_H^+ 7.0$. The determination of the original acidity of freshly made infusions of various tanning materials is of importance, as it may safely be predicted that they will vary considerably. From the above figures (4.6 cc. of N/10 alkali per 100 cc. liquor) it will be seen that the acidity of the stronger liquors (*e.g.*, Table IV) is partly due to the tannin present. We have come to the conclusion that the free acidity of tan liquors for the purposes of the tanner is very accurately shown, or best shown for control purposes, by means of Procter's lime-water method. Where the liquors contain little tannin a small quantity of a 1 per cent. solution of quebracho extract may be added, and a small correction made for the acidity of this.

In the following tables (3-7) we give results obtained with actual tan liquors. The hydrion concentration of the acid is probably influenced by the presence in the liquors of other salts besides those of calcium. That these are present is shown by the alkalinity of the ash produced on evaporating and igniting some of the liquors. The alkalinity is greater than that due to the calcium salts found by precipitation as oxalate.

In titrating some of the heavy leather liquors containing lime

[1] P_H^+ is the exponent of hydrion concentration. See Sörensen, *loc. cit.*

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salts it was noticed that a turbidity was produced before neutrality, as indicated by the potential difference, was reached. This precipitate was produced at 0.65 to 0.67 volts potential difference and apparently while it was being formed the voltage remained constant during the addition of more alkali, the potential difference afterwards rising to 0.69, when sufficient alkali had been added. The precipitate thus appears to be the lime salts thrown out of solution by the neutralization of the acid which had hitherto kept them in solution. This supposition would also account for the constancy of the potential difference during the precipitation. This precipitation is only observed with the weaker liquors, in the case of the liquors stronger in tannin, the precipitate is colloidal, and appears at no definite point.

In conclusion, we give the complete neutralization curves of

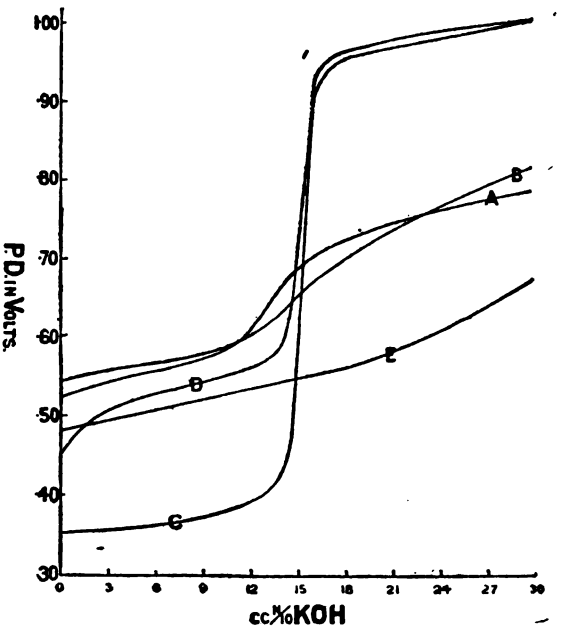

Fig. 2.

A—Light leather tan liquor. B—1st suspender sole leather liquor. C—Deci-normal sulphuric acid. D—Deci-normal acetic acid. E—"10-day liquor," from sole leather yard.

three tan liquors, together with those obtained for N/10 sulphuric acid, and N/10 acetic acid. It will be seen that the curves for

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the tan liquors differ from each other in a very appreciable manner, and it will be realized that in making these differences manifest, the electro-metric method is giving information which can be obtained from no other process of titration. It should be noted that slight differences in the curve may be produced by the traces of carbonic acid in the caustic potash used for the titration. It will be realized that the indications of the electro-metric method have a degree of certainty and objectiveness which is not approached by other methods. It still remains, however, to interpret the results in terms of direct value to the tanner.

TABLE III.

Description of liquor	Normality of acids by titration	Initial P. D. in volts	Lime in grams per liter	Normality of calcium salts	Normality of hydrion
1 First suspender.....	0.084	0.560	1.870	0.067	0.000020
2 Intermediate round.....	0.305	0.498	0.720	0.026	0.000229
3 Last layer.....	0.375	0.494	1.050	0.037	0.000275
4 End suspender	0.044	0.500	1.2250	0.044	0.000209
5 Middle suspender.....	0.076	0.500	0.9250	0.033	0.000209
6 Top suspender	0.136	0.480	1.0000	0.036	0.000478
7 Weak pit (light leather)..	0.070	0.568	1.550	0.055	0.000014
8 Strong pit (light leather) .	0.106	0.519	0.925	0.033	0.000066
Deci-normal acetic acid ...	0.100	0.448	..	..	0.001333

TABLE IV.—TAN LIQUORS FROM A SOLE LEATHER TANNERY.

No.	Barkometer degrees	Tannin grs. per 100 cc.	Initial P. D. volts	P_H^+	N/10 alkali per 10 cc. liq. by electrometric method	Cc. N/10 lime water	$\frac{E^1}{L}$	
1	20.8	0.67	0.560	4.7	8.4	7.2	1.17	Cloudy at 7.2 cc. N/10 KOH
2	36.8	2.88	0.522	4.05	14.7	11.0	1.34	Cloudy at 13.3 cc. N/10 KOH
3	46.0	4.80	0.511	3.86	19.3	13.4	1.44	Cloudy at 17.2 0.675 v.
4	62.5	8.97	0.500	3.68	27.3	16.4	1.67	Darkened, but no pp. apparently below 0.69 v.
5	67.4	9.52	0.499	3.65	29.1	16.8	1.74	
6	71.1	9.91	0.498	3.64	30.5	17.1	1.79	
7	74.4	10.56	0.499	3.65	33.5	19.1	1.76	
8	86.5	13.07	0.494	3.56	35.3	20.6	1.71	
9	94.7	16.96	0.490	3.50	36.5	20.7	1.76	
10	96.3	15.65	0.494	3.56	37.5	22.2	1.70	

Nos. 1 and 2 = suspenders. Nos 5 and 6 = intermediate rounds.
Nos. 3 and 4 = handlers. Nos. 7-10 = layers.

[1] Ratio of figures obtained by electrometric and lime water methods.

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TABLE V.—SUSPENDER LIQUORS FROM SOLE LEATHER TANNERY.

Description of liquor	Tannin grms. per liter	Lime water method	N/10 potash till turbid	N/10 potash to 0.69 volts	Initial P. D. in volts	P_H^+
End suspender 15°....	9.3	2.95	3.04	4.4	0.50	3.68
Middle suspender 20°..	13.4	5.4	5.94	7.66	0.50	3.68
Top suspender 28°	20.2	7.55	8.44	13.6	0.47	3.15

Acidity expressed as N/10 alkali per 10 cc. tan liquor.

TABLE VI.—TAN LIQUORS FROM SOLE LEATHER TANNERY.

No.	Description of liquor	Tannin in grms. per 100 cc.	Initial P. D. volts	P_H^+	Cc. N/10 potash per 10 cc. liq. (to 0.690 v.)	
81	Color pit....	0.89	0.545	4.44	7.3	Faintly turbid at 6.2 cc. (0.658 v.)
82	6 day liquor.	2.14	0.520	4.02	10.9	Cloudy at 9.6 cc. (0.660 v.)
83	10 day liquor	4.58	0.494	3.56	20.9	Cloudy at 0.690 v.
84	5 weeks liquor	8.64	0.484	3.40	29.6	No turbidity with excess of alkali

TABLE VII.—LIGHT LEATHER LIQUORS.

No.	Tannin in grms. per 100 cc.	Initial P. D. volts	P_H^+	Cc. N/10 potash per 10 cc. to 0.690 v.
1	0.73	0.568	4.84	7.0
2	0.96	0.540	4.34	9.1
3	1.45	0.525	4.10	10.0
4	1.80	0.533	4.24	10.6
5	2.03	0.530	4.20	10.3
6	2.09	0.532	4.25	10.45
7	2.31	0.532	4.25	10.65

We would suggest that the research laboratories of the leather industry might well undertake this matter, and that by continuous investigation much valuable information would undoubtedly be accumulated. We may say that the Leather Industries Department of the University of Leeds has already taken a step in this direction.

DISCUSSION.

PROF. PROCTER said that Mr. Seymour-Jones and he had found that the addition of sodium chloride to very dilute acetic acid slightly increased the hydrion concentration of the mixture, indicating the actual presence of free hydrochloric acid liberated by the much weaker acetic, and confirming the hypothesis of a quadruple equilibrium of acetic and hydrochloric acid and sodium acetate and chloride.

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He agreed with the authors that the apparent alkalinity of sodium acetate was due to hydrolysis of the normal salt. He confirmed the usual presence of lactones in commercial lactic acid, and mentioned a recent patent of Eberle for their use as neutral deliming agents, since in presence of lime they formed lactates.

He suggested that as the swelling power of liquors was too complicated a function to be determined chemically, it was possible that empirical results might be obtained by soaking a weighed portion of thin sheet gelatine in the liquid for 24 hours or some other definite time, and weighing or measuring the absorption of liquid, since the tannin did not penetrate but merely formed a thin semipermeable layer on the surface.

He also mentioned that the perforated chimneys often used for incandescent burners formed very effective centrifugal stirrers if inverted in a beaker so that the holes were below the surface of the liquid and rotated.

Dr. E. Stiasny thought the acidity of tannins themselves, as found by the authors, might not have any influence on the swellings of hides in the suspenders, because the low hydrion concentration would still be naturally lowered by the presence of the stronger organic acids (lactic and acetic acids) which exerted an inhibitory effect on the ionization of the tannic acids.

Mr. J. M. Wilkie asked with regard to the water used in the experiments, had the authors taken any special precautions to ensure the absence of carbon dioxide? He had found considerable difficulty in getting water free from carbon dioxide and had always found that, though boiled in Jena glass, such boiled out water possessed a distinct acidity towards phenolphthalein. Were the salts used in the research the ordinary pure chemicals of commerce, or had any precautions been taken to ensure that they were of the correct composition? Finally, it was not unlikely that the discrepancies observed with lactic acid were due to the presence of lactones which it was well known were present in the ordinary lactic acids of commerce, so that by direct titration, low results would be obtained.

Mr. R. A. Seymour-Jones remarked that the work done by Professor Procter and himself indicated a "plumping" limit of about 10^{-5} N hydrion concentration. Had the authors deter-

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mined that point? Had they made any experiments on quadruple equilibria, as interesting results had been obtained at Leeds? Could they reduce the hydrion concentration of their "conductivity" water below $10^{-6.2}$ N by the ordinary means of purification?

Mr. Wood said, in reply to Dr. Stiasny, the authors did not for a moment imagine that the acidity of the tannins had any swelling action on the skins; they merely drew attention to the fact that the tannins increase the quantity of potash consumed to bring the liquor to the neutral point. The hydrion concentration named by Mr. Seymour-Jones, namely, 10^{-5} normal, would no doubt be somewhere about the limit of swelling power, although the point at which the authors found the liquid go cloudy during titration with potash was about $10^{-6.2}$.

With regard to the water used, no special precautions to expel carbon dioxide were taken beyond boiling, so that it was certainly not so pure as $10^{-6.2}$. In reply to Mr. Wilkie, the chemicals used were Kahlbaum's pure salts and acids. They thought it sufficient to use the purest salts they could procure commercially rather than to give figures for those which could only be prepared by an excessive expenditure of time and trouble. His suggestion as to the presence of lactones in the lactic acid being the cause of the discrepancy from theory was probably the correct one.

With reference to Professor Procter's remarks, they had tried the experiment of adding salt to acetic acid at an early stage of the work, and called attention to it in the paper. They noticed a slightly increased hydrion concentration, but had not followed up the subject. What he said about quadruple equilibria was extremely important to the tanner, because he might get free mineral acid in his leather quite unwittingly.

THE STRENGTH OF ACIDS.[1]

By Prof. H. R. Procter.

A firm of tanners wrote me the other day with regard to deliming "We note your remarks *re* formic acid being cheaper than lactic: at the moment we are paying 27/-per cwt. for

[1] Tanner's Year-book, 1911.

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lactic, and 47/6 for the formic, and so cannot understand your statement." Now, in the first place, the lactic acid was only 47 per cent., while the formic was 88 per cent., so that at the prices quoted 100 per cent. lactic acid cost 57/4, while 100 per cent. formic was 54/-; and, secondly, of 100 per cent. acids, 90-lbs. of lactic acid and only 46-lbs. of formic are required to neutralize and dissolve 28-lbs. of lime. Thus, to dissolve 1-lb. of lime, the cost of lactic would be 19.8d. and of formic only 9½d. It will be observed that ignorance of these points may prove somewhat costly; but while even chemists use the word "strength" in three distinct senses, it is more or less excusable in the business man. We have already used the word in the sense of percentage, and we might also in that of lime-dissolving power, but the third is equally important. The cost of removing 1-lb. of lime with commercial hydrochloric acid is only about 1.4d., and with sulphuric acid 0.8d., but we hesitate to use these because they are too "strong"—the slightest excess would overswell the hides and produce bad leather; while the organic acids are comparatively safe in use because they are "weak." If we make solutions of the various acids of such strength that 1,000 gallons of each will dissolve 28-lbs. of lime (the chemist will recognize these as of N/10 strength), we shall find great differences as regards sourness, swelling power and other characteristics of acids as such. Until recent years no reason for this could be assigned, but we now know not only the cause, but, to a considerable extent, how to control it. All acids owe their acidity to the fact that they contain a loosely combined hydrogen "ion" (a single atom of hydrogen with a + electrical charge), and the strength of the acid in the last-named sense depends on the proportion of these which become separated from their companion acid-ions in solution. In hydrochloric acid almost all are free and active, even in strong solution; while in acetic the proportion is quite trifling, though it increases on dilution. The case may perhaps be best understood by the analogy to lime, which, though a very strong alkali, acts quite mildly on hide because of its very slight solubility, so that we can use it in great excess, which forms a reserve to keep up the strength of the liquor, as that first dissolved is absorbed by the hides. All the acids named mix freely with water, but only the strong

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ones become completely "dissolved" or ionized in any reasonable dilution, and it is only the ionized portion which acts. As, however, the ionized portion is used up, its strength is maintained by the ionization of a further quantity, so that an acid like acetic, while acting mildly and slowly has large reserves of "undissolved" acid on which to draw, while the whole of the hydrochloric acid acts at once. In this sense, hydrochloric and sulphuric acid are irrepressible, but the strength of the organic acids can be controlled on the following principle. If we imagine a ball-room with an equal number of each sex and in which the men represent the hydrogen-ions, a large proportion will be paired and gyrating harmlessly, and it is only the small number sitting out who are of any account in making new combinations. In acetic acid the number of pairs of atoms "sitting out" is very small in any case, but it will be still further reduced if we bring in a sufficient number of girls and their chaperons. The latter do not count for our purpose, nor do the superfluous girls, but the men may all be supposed to find partners. To drop parables, if to a solution of acetic acid A-H′ we add sodium acetate A-Na′ we bring in a large quantity of additional acet-ions A; and the law is that the number of free A. multiplied by that of free H′ bears a constant proportion to the quantity of un-ionized acid, so that as A increases, H diminishes. The practical outcome of this is that you can weaken the acid as much as you desire by adding its own salt, and if this is done sufficiently, formic acid will act as mildly as acetic. Generally speaking such an addition is only necessary at the outset, since in deliming hides lime salts are constantly formed, and all that is needed is not to change the water too much if milder action is desired. It is impossible to regulate the strength of strong acids in this way, and the familiar pickling of salt depends on other reasons, but the addition of an organic salt, such as sodium acetate in sufficient quantity to hydrochloric acid will reduce its strength to that of acetic, so that, beginning with one of the weak organic acids, perfectly safe deliming may be done by adding hydrochloric or sulphuric acid, so long as the acetate, etc., is in excess and the water is not much changed; but of course some degree of chemical control is required for safety.

The following little table gives the cost of dissolving 1-lb.

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of lime at present approximate prices of the various acids and the figures under K their approximate relative "strength," while under Eq. the weight in lbs. of 100 per cent. acid required to dissolve 28-lbs. of lime may be understood. Ordinary wet limed hides, unhaired and fleshed, only contain about 4-lbs. lime per 1,000-lbs. wet weight:—

COST OF ACIDS TO REMOVE 1 LB. LIME.

Acid	Eq.	K.	Cost per cwt. s.	d.	Strength per cent.	Cost for 1 lb. CaO d.
Hydrochloric ..	36.5	Say 200	3	3	31.5	1.4
Sulphuric	49.0	Say 200	4	0	95.0	0.8
Oxalic	63.0	0.1	30	4	99.9	8.1
Formic.....	46.0	0.0214	35	0	87.4	7.0
Lactic	90.0	0.0138	26	0	49.7	18.0
Acetic.....	60.0	0.0018	18	0	40.0	10.0
Butyric.....	88.0	0.00115	21	0	82.8	8.0
Boracic.....	62.0	0.00000001	27	0	99.0	6.5

THE NEUTRALIZATION OF CHROME LEATHER.[1]

By Edmund Stiasny.

The modern manufacturer of chrome leather, especially of box calf, willow calf and glazed kid, has to produce the very best leather both as to quality and appearance, and if he desires to be successful in the competition which recently has become so vigorous through the import of excellent leather from America, France and Germany, there is not a single process from the soaking of the raw material to the finishing of the leather which does not demand the most careful attention if a perfect product is to be put on the market. The least carelessness, even in such operations as damping before staking, or oiling before drying, etc., could upset all the trouble taken in the other processes. The neutralizing of the chromed skins is also important, and any neglect in this small part of the whole manufacture might have a very bad effect on the quality and appearance of the final product.

It is generally known that the neutralizing of chrome leather serves the purpose of removing all free acid which is present in the leather after chroming, and which cannot be washed out

[1] Tanners' Year-book, 1911.

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completely by mere drumming with water. It is also known that chrome leather which contains free acid will cause troubles in the process of fat-liquoring, because the free acid will decompose the soap and produce free fatty acids which may combine with the soluble part of the absorbed chrome salts, forming chrome soaps of a most unpleasant, sticky and smeary character. Such chromed soaps are not easily got rid of, and the whole finished work is rendered unsatisfactory by their presence on the grain. Moreover, a considerable amount of free mineral acid in the leather will attack the fiber of the leather during drying, and a tenderness or cracking of the grain will be the consequence. Another fault which is not seen before the goods are finished and stored for some time is the spueing which may be due to so many different causes, one of which is the presence of acid in chrome leather.

It would be quite a simple thing to avoid all these troubles by removing the last traces of acid if we could use an excess of alkali, but this is not permissible, as the danger of "over-neutralization" is perhaps even greater than that of leaving a trace of acid in the skin. The effect of excess of alkali may be explained in different ways: it may be that in neutralizing the free acid the alkali acts on the basic chrome salt which has been absorbed during the course of tannage so that chrome hydrate is formed which produces a poor leather; or that the excess of alkali attacks the fiber itself, which is very sensitive to alkaline liquors and becomes dry and hard. Whatever be the real reason, the practical result of over-neutralization is to produce a poor, hard and tinny leather.

Thus, steering between Scylla and Charybdis, the tanner has to hit the right moment when free acid is just removed, but no further action has started. Frequent testing of a fresh cut with litmus paper is the only help for successful work, and many practical men in doing so stop the process when a small streak of the cut still is slightly acid, since they are more afraid of over-neutralizing than of the effect of a small amount of remaining acid. These tanners obviously expect some neutralizing effect from the subsequent dyeing process due to the small amount of soda or ammonia which usually is added to the logwood solution; they also trust that the fat-liquor which contains a trifle

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of borax or soda will accomplish the neutralizing, and that the last traces of acid in the very middle of the skin may be removed by the soap itself, which, forming free fatty acids and chrome soaps, acts to some extent as a filling and a softening agent on the leather. It is clear that the judgment of such a small amount of acid as can be removed in this way will give some difficulty to the foreman, who depends entirely on the color test on litmus paper, this test being in no way a quantitative one, and it is probable that the foreman will sometimes go wrong by leaving far too much acid in the leather and thus cause all the trouble which has been mentioned above.

There is still another point worth mentioning, namely, the speed of the neutralization process. It is not advisable that large amounts of free acid in the fiber should be suddenly neutralized by an alkali of considerable strength. This is especially so in using carbonates; the carbon-dioxide produced between the fibers exerts a mechanical action and causes a loose or pipy grain. This danger can to some extent be avoided by a thorough washing of the leather with water in order to remove a greater excess of the acid previous to the action of the alkali.

There are a great number of substances used in different tanneries for neutralizing chrome leather, borax probably being the commonest; but sodium carbonate, sodium hydric carbonate, calcium and magnesium carbonate, sodium phosphates, sodium silicate, ammonia, etc., are also used, and Eitner has some time ago even advocated sodium sulphide. While the stronger of the alkaline materials mentioned, like sodium carbonate, ammonia, sodium silicate, and especially sodium sulphide, require the greatest care, and can easily cause considerable harm to the leather; others again, owing to their little solubility, like calcium carbonate (magnesium carbonate is a little more soluble) act rather too slowly and not completely enough in the time which can be given by the practical tanner. Even borax and sodium phosphate, the most suitable of the above substances, require considerable care in application if the exact point of neutralization is to reached.

The fact, therefore, is of some interest to the practical tanner that we can easily carry out the process of neutralization in a safe and simple way by applying a mixture of two substances,

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the one of which is the alkali, and the other a kind of "controller," which only allows a very small amount of this alkali to be active at a time and replaced as soon as it is used in the process. Such a mixture would represent the necessary alkali for complete neutralization and still act like an extremely dilute solution. We can even use such a mixture in excess because it will have no bad effect on the completely neutralized leather according to the extreme weakness of active alkali. Moreover, we can regulate the action of the mixture by varying the quantity of the controller which we add to the sufficient amount of alkali for complete neutralization. A suitable mixture of this kind for practical purposes is sodium carbonate and ammonium chloride, in which the sodium carbonate alone acts like an alkali of considerable strength; but by the addition of the ammonium chloride this alkaline action is diminished to a very great extent, the diminution being in accordance with the amount of ammonium chloride added. On the basis of some well-known principles of physical chemistry, we can easily calculate the degree of active alkalinity of a given mixture of these two substances, but this cannot well be discussed here in detail. It need but be said that the sodium carbonate reacts with the ammonium chloride, giving a certain amount of ammonia, and that the strength of this ammonia solution is materially diminished by the presence of the excess of ammonium chloride. During the process of neutralization the small amount of active ammonia is used up, reformed and used again, and so on; and the ammonia sulphate which is formed by the process acts as an additional controller, so that the neutralizing process is rendered milder and slower as it goes on, and the remaining liquor finally becomes far too weak to do any harm to the leather.

A series of practical trials in the experimental tannery of the Leather Department of the Leeds University have shown that equal parts of washing soda and ammonium chloride represent a suitable mixture. It is advisable to take 2 per cent. of each (on the shaved weight) and drum the goods with this solution for about ten to fifteen minutes, then to add another mixture of 2 per cent. washing soda and 2 per cent. of ammonium chloride, and to continue drumming for fifteen to twenty minutes. If after this time the cut of the thickest part of the leather should

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not be entirely neutral to litmus paper, the drumming should be continued or another portion of the mixture (2 per cent. of each) added, there being no danger of using an excess. After neutralizing, the goods must be washed thoroughly with cold water in order to remove all soluble salts.

Chrome leather which has been treated in this way will present no difficulty in fat-liquoring, and will have no tendency to spue, provided there are no other reasons for this defect, as weak grain, unsuitable fat-liquoring, etc.

The mixture of washing soda and ammonium chloride can equally be recommended for stripping vegetable-tanned leather before chroming (semi-chrome tannage). For this purpose 4 to 5 per cent. of both washing soda and ammonium chloride may be used, and the leather washed afterwards in the usual way.

BOOK NOTICES.

Fortschritte in der Gerbereichemie. Dr. Franz Ch. Neuner, Vienna. Published by Theodor Steinkopf, Dresden. Price M. 1.80. ($0.45).

A nearly complete translation of this review of the progress of leather chemistry was published in the JOURNAL for May, 1911. This reprint is in convenient form, very fully indexed.

Buyer's Guide for Leather Manufacturers. Deming and Rogers Publishing Co., Boston. $2. This little book has 125 pages (beside advertisements), the size of the page being about 3 by 6 inches. It undertakes to be a directory of leather manufacturers and dealers in the various kinds of raw materials and supplies used in the manufacture of leather, and also several allied lines, for the whole United States. An appendix gives the officers of the following associations:

National Association of Tanners.
Morocco Manufacturers' Association.
American Leather Chemists Association.
Patent and Enamel Leather Manufacturers' Association.
Lace Leather Manufacturers' Association.
National Association of Leather Belting Manufacturers.

In two, at least, of the directories for the various branches of the trade there are important omissions.

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The Tanners' Year Book, 1911.

The Tanners' Year-Book is the organ of the United Tanners' Federations of Great Britain and Ireland. It was compiled by C. E. and J. G. Parker, and published by the Leather Trades Co., London. It may be obtained from W. B. Moston, Penketh near Warrington, for two shillings, nine pence. The matters contained in its 170 pages is as follows:

Lists of officers and members of the various federations.

Reports of the activities of the federations.

Tables of imports and exports.

The Strength of Acids, by H. R. Procter, (published in this issue of the JOURNAL).

The British Leather Trade, by E. H. Dickinson.

Mr. Dickinson points out that with the industrial development of China, Japan and India hide exports from those countries must diminish, and this change must be offset by increasing the area now devoted to cattle raising in South Africa and elsewhere.

Foreign Investments and their Effect on Home Industry, by C. E. Parker.

The Use of Quinone in the Tannage of Sole Leather, by Prof. L. Meunier.

Non-tannins and Pseudo-tannins, by Dr. R. Lepetit.

The Neutralization of Chrome Leather, by E. Stiasny, (published in this issue of the JOURNAL).

Notes from Ireland, by E. J. Long.

Roller Leather for Cotton Spinning, by Charles Prescott.

Tanning in Afghanistan, by E. T. Thornton.

Chemistry of Tanning, Extract of Year's Work, by Stanley Hirst.

That Wet Bean-feast, by H. G. Crockett, of LEATHER.

Notes on Valonia.

Smoke Tannage in China.

The Natural Acids of the Tan-liquors and their Influence in Leather Manufacture, by R. A. Seymour-Jones.

The Leather Binding of the New Encyclopedia Britannica, by C. F. Clay.

Travellers in the Leather Trade, by H. O. Hinton.

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Present Position of the Leather Industries in Spain, by Alberto Fontana.

Quebracho Duties in Germany.

American Hide and Leather Company and Subsidiary Companies.

Earning Power of British Railways.

The Port of London.

Mechanical and Horse Haulage.

Argentina. In 1858 cattle formed 25 per cent. of the total wealth of Argentina, but in 1885 only 18 per cent. The total value of cattle, however, had increased enormously. Since 1885 the average value per head has increased from $13 to $32. The export of frozen beef seems to be largely responsible for this rise. The extending use of alfalfa is making it possible to maintain several times as many cattle on a given area as formerly. The total value of quebracho exports in 1908 was $6,000,000.

Labor Exchanges, by R. Williams.

(Further extracts from several of the above articles will appear in future numbers of the JOURNAL).

Le Cuir for August 1st, is a special Exposition Number, giving a list of the French leather exhibits to be shown at the Turin Exposition.

ABSTRACTS.

The Determination of Free Acids in Oils and Fats, Particularly in Mineral Lubricating Oils. H. LOEBELL *Chem.-Ztg.*, 1911, 276-7.—The usual solvent, an alcohol-ether mixture (1:4) is unsuited, since it permits only a very slight dissociation of acids. It is well known that both components contain a certain amount of organic acids, yet on addition of alkali blue to the blank solvent, a dull violet results instead of the pure blue corresponding to an excess of H-ions; with more indicator a precipitate settles and the supernatant liquor is reddish in spite of the acids present. Phenolphthalein gives a sharper end-point, but this is due to the lack of color in the non-ionized indicator and it is necessary to over-titrate with alkali to reach a marked red. The author finds a more suitable solvent in a mixture of 2 vols. benzol, 1 vol. 96 per cent. alcohol. With alkali blue the color change is sharp, blue to red. The principal experimental data are:—

I. *Alkali Blue Indicator.*—For analysis, 10 cc. of a mixture of 500 grams liquid paraffine with 5 grams oleic acid were titrated.

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In alcohol-ether			In benzol-alcohol		
Color change	Per cent. acid as SO_3	Oleic acid	Color change	Per cent. acid as SO_3	Oleic acid
Blue violet	0.113	0.796	Blue red..	0.134	0.945
Violet claret	0.114	0.803			
Unchanged	0.130	0.916			
Blue bl. viol.	0.118	0.831		0.134	0.945
Bl. viol., red viol.	0.138	0.972			
Claret	0.146	1.025		0.134	0.945
Bl. viol., red viol.	0.111	0.783		0.134	0.945

The oleic acid used was slightly impure.

II. *Phenolphthalein Indicator.*—A mixture of red brown machine oil with pure oleic acid, known to contain 0.144 per cent. SO_3 = 1.014 oleic acid was used.

In alcohol-ether Change, yellow-red yellow, indistinct Per cent. acid reckoned as		In benzol-alcohol Change, blue-red, sharp Per cent. acid reckoned as	
SO_3	Oleic acid	SO_3	Oleic acid
0.147	1.036	0.143	1.008
0.152	1.072	0.144	1.014
0.147	1.036	0.142	1.001
		0.144	1.014

Experiments were also made titrating a benzol-alcohol solution with 0.1 *N* $Ba(OH)_2$, phenolphthalein indicator, with satisfactory results.

W. J. K.

The Determination of Trypsin in Dog Dung. G. Eberle and L. Krall, *Collegium,* 1911, 201.—Simon, (*Beryl. Berichte,* 1893) first prepared trypsin as a bating agent; the application of pancreatin, in which trypsin is the essential active ingredient, was studied by Wood. (*Jour. Soc. Chem. Ind.,* 1894, 218; 1898, 1010; 1899, 91). This substance has not received much attention in leather industry, principally because of the use of Popp and Becker's "Erodin," a bacterial product prepared from dog dung. Also it has been assumed that trypsin is not present in dog dung. The authors have, however, now proved its presence.

The first series of experiments demonstrated the presence of proteolytic enzymes. Two methods were employed: (1) that of Gross, which uses as reagent a soda solution of pure fat-free casein; this is broken down by proteolytic enzymes giving products which remain in solution on addition of acetic acid. Unlike the gelatine test, it may be used at the high temperatures (36-40° C.) used in bating; (2) the method of Giessen (*Dissert.,* Bonn, 1909). A drop of the suspected solution is transferred by a platinum loop to a sterilized gelatine plate and after a time the degree of corrosion compared with that produced by standard pancreatin solution. Positive results were obtained by the authors on testing dog dung either fresh, heated 8 days at 37°, or allowed to stand moist 8 days to 2 months; the action diminished on storage.

To prove the presence of trypsin, use was made of the principle that pancreatin is an antigen, or a substance which introduced into the animal sys-

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tem causes the generation of a counteracting substance. If the anti-pancreatin accumulating in the blood serum of an animal thus treated is found to prevent the proteolytic action of dog dung, then trypsin is present. Pure pancreatin (Merck) was injected beneath the skin and into the abdominal cavity of guinea pigs and after 14 days the blood serum was isolated for experiment. It was found itself to have no digestive action on gelatine when treated by Giessen's test; a small amount added to a 5 per cent. pancreatin solution completely inhibited its digestive action. The same result was obtained with extracts of fresh and old dog dung; the original solutions showed marked proteolytic action on gelatine plates but after addition of the serum, no effect was produced on the gelatine, even after 6 hours. W. J. K.

Reagent for Chromium. PAUL KOENIG. *Chem.-Ztg.*, 1911, 277-8.—This is the Na salt of 1,8-dioxynaphthalene 3,6-disulphonic acid (chromotropic acid, chromogen I); it serves to detect and estimate mere traces of Cr, in plant ash, etc. The Cr must be present as acid, first oxidizing if necessary. The reagent gives a cherry red to dark red violet color. Ferric salts give a green but this interference may be prevented by addition of phosphoric acid. W. J. K.

Tannin Extraction. G. METZGES. *Ledertechn. Rundschau*, 1911, 105-6. —O. Kohlrausch first introduced (1880) systematic extraction in batteries; closed tubs were used under a hydraulic pressure of about 1 atm. and are yet in use, although on the large scale copper diffusers are generally employed. In such an extraction, two operations take place: (1) direct solution of the finely divided material by contact and equalizing of the total solution by circulation; (2) solution of material within the unruptured cells and diffusion through the membranes. This last, from the colloidal nature of tannin, is very slow.

The devices employed for shortening the time of extraction include high temperature and fine grinding of material which exposes more opened cells to surface solution and reduces the time of diffusion by making the cell-complex smaller. The extraction of hard material like wood is promoted by a preliminary softening, either by soaking or a prolonged treatment in additional batteries. The use of compressed air for transmission of extracts is an improvement over high pressure steam.
W. J. K.

What Role Does the Acid Play in Tanning? B. KOHNSTEIN. *Collegium*, 1911, 244-7.—The usual statement in the books on the theory and practice of tanning, is that acids plump or swell the hide, promoting its absorption of tannin. The author would supplement this dictum with the proviso that the manner in which the hide has been prepared for tannage must be considered as it is possible that the reverse of the desired effect may be produced. Dreaper (*Zeit. chem. u. Ind. d. Kolloide*, 8, Heft 5) explains the variations in speed of tannage as dependent on the size of the tannin molecule, the large molecules diffusing slowly; in

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aqueous solution, for example, the molecule is compound, say nine simple molecules condensed while in acetic acid solution tannin is monomolecular. The author grants this explanation may apply to pure tannic acid, but not to the conditions of practical tannage. It is indisputable that a swollen hide absorbs tannin more rapidly, but an essential condition is that the hide itself be free from acid. In the practical tannage of vache leather it has been often observed that sweet liquors give much better results in the foretannage than when strongly acid liquors are used. If pine tanned hides which have already been treated in the foretannage with strong acid liquor be layered with pine and made still more acid, the gain in weight will be slight nor will it be bettered by steeping with sweet liquors or extracts. An acid tanned leather will likewise fail to tan through in the drum.

If acid be added to an extract easily soluble in cold water, a precipitate is formed; besides the phlobaphenes, resins and tans are thrown out. Likewise on the immersion of a plumped hide saturated with acid in a sweet extract solution, the membranes become coated with slime and the tannage proceeds slowly. This explains why in America in the manufacture of the so-called acid leather, the acid plumping is followed by a cold bath in which water replaces the acid within the hide. The American tanner follows the principle—"an acid free swollen hide absorbs tannin easier and quicker."

The practical tanner applies the precipitating effect of acids to lessen the loss of tans in washing. In the final treatment of an extract saturated leather, an oxalic acid bath is used. W. J. K.

Furniture Leather. FERD. KOHL. *Ledertechn. Rundschau*, 1911, 81-3, 89-91, 99-100.—For raw material good sorting is needed; for colored leathers, good, clean grained hides are needed; salted hides, which are used the most, should be carefully cooled if stored during the warm season and well drained from brine. For soaking, 2 days generally suffices; the water should be often changed. Liming should be very gradual and systematic, best with mechanical stirring; time, 4-6 days. After washing, shaving and splitting, the hides are de-limed with hydrochloric or oxalic acid at 28-30° C. The tannage is begun with care, reeling through weak oak liquor for 2 hours, continuing in suspender vats. The tannage is complete in about 3 weeks. For antique leather, the hides go soon into strong liquors which produce the peculiar shrunken grain. After a borax treatment, an after tannage with sumac follows, then oiling and drying. Details are given of dyeing, currying, and the production of antique and velvet leathers. W. J. K.

The Examination and Valuation of Preserved Egg-Yolk (Barreled Eggs). DR. WELMART, Vienna. *Gerber Courier*, May 27, 1911.—For the purpose of glace and kid leather tannage, egg-yolks, preserved with NaCl and borax are used. By drumming, the albumen is forced into the hide and by simultaneous tanning is fixed on the hide-fiber. In addition the yolk-oil contained in the egg-yolks coöperates in the tanning and likewise im-

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parts a certain capacity for water-resistance to the leather. Concerning the action of egg-yolks in the tanning process diverse explanations have been offered.[1]

Barreled eggs with a water content of 50 per cent. and an addition of 15 per cent. NaCl should have the following composition:—

	Per cent.
Water	50
NaCl	15
Other ashy constituents	2
Yolk-oil	20
Albuminoid	13

The oil in the egg-yolk is contained in a very fine emulsion, microscopically in the form of minute balls which are separated by the albuminoid covering. Regarded microscopically a certain similarity exists between yolk-oil and milk-fat. In white-leather degras, the fat is to be found in the most perfect emulsion. The addition of a strange fat or oil is to be regarded as an adulteration, since added fat never allows itself to be brought into an emulsion so homogeneously.

The barreled eggs are dessicated with sand and the oil obtained through extraction with ether, petroleum ether, chloroform, carbon tetrachloride, or carbon bisulphide. For pure oil, the constants are:—

	Chicken eggs per cent.	Duck eggs per cent.
Iodine value	50—72	36—38
Phosphoric acid	2.2 —2.4	1.8—2.0
Unsaponifiable matter	0.15—0.25	2.5—2.8
Refraction index	1.476	... ...
Saponification value	170—180	175—178

The ratio between yolk-oil and albumen will be found in the same way as in the case of natural egg-yolk. A lack of fat denotes adulteration with the white of eggs or other materials. The natural egg-yolk shows from a number of analyses the following average composition:—

	Per cent.
Water	50.8
Albumin	16.0
Yolk-oil	32.0
Non-nitrogenous material	0.1
Salts	1.1

Dried egg-yolk, which has been employed as an equivalent for barreled eggs, on the basis of the water-free material shows the following average composition:—

	Per cent.
NaCl	1.5
Phosphoric acid	3.5
Yolk-oil	61.5
Albumen	33.5

[1] See Knapp, Dingler's Polytechnical Journal, 181, 311.

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From the high price of barreled eggs and the great demand for glacé and chevreaux leather dressing it is not to be wondered at if the barreled eggs should be adulterated excessively, with much salt, strange oils, and animal or vegetable albumen.

The detection of an adulteration with salt or strange oils offers to the trade chemist little difficulty. The ash-contents of the egg and the constants for the yoke-oil give a safe test of the pureness of the product. On the contrary the detection of the presence of added animal or vegetable albumen was not thought feasible until a short time ago.

A practical method for distinguishing different albumens has been worked out by Uhlenhut and Weidanz, and published at Jena, 1909.

Vat-tannage. Lecture by M. NIHOUL, Professor of Industrial Chemistry at the University of Liege, and Director of the Tanning School at Liege. *Le Cuir,* Vol. IV, No. 10, p. 307.—"Non-tans" include many and various substances. They are at first mainly sugars, glucosides or gums derived from the plant. The gums and glucosides are largely converted into sugars by the action of zymases in the liquor. The liquor is a favorable medium for the growth of microörganisms, containing beside organic substances potash, phosphates and other mineral matters, and nitrogen furnished by the hide. The microbes derived from the air and other sources set up in the liquor various fermentations. Five types are mentioned, three normal and two harmful. (*a*) Alcoholic fermentation is due to the action of yeasts on the sugars of the liquor. This fermentation is able to proceed at a low temperature, 5° to 6° C. (41° to 43° F.) sufficing. It is hard to show the presence of alcohol in tan liquors, because it is changed into acetic acid as fast as made. (*b*) Acetic fermentation is brought about by the same organisms which produce vinegar from fruit juices and malted grains. This fermentation begins at about 10° C. (50° F.) and is promoted by access of air. (*c*) Lactic fermentation is caused by many organisms, some of which are abundant in the air. It takes place at temperatures from 10° to 12° C. (50° to 54° F.) but generally proceeds best at from 30° to 35° C. (86° to 95° F.). These organisms act upon the glucoses of the liquor, producing two molecules of lactic acid by the splitting up of one molecule of glucose. This acid is antiseptic in the sense that it hinders the growth of many disease germs. Its presence in the vats is desired in the making of light leathers, while acetic acid is preferred in the making of heavy leathers.

So long as these three fermentations only go on in the liquors, the series of vats may be considered to be in a healthy and normal condition. The action of the ferments is progressive. As the quantity of tannin in the liquor decreases, the proportion of acid to tannin increases; and as the hides advance into stronger liquors they meet with a less and less proportion of acid. In the latter vats of the series the acid is not so much needed to maintain plumpness in order to permit the penetration of the tannin.

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Unfortunately other microörganisms may develop in the liquors, and of these two are particularly objectionable, those which cause butyric and gallic fermentation. The former is carried on at the expense of the lactic acid of the liquor, two molecules of lactic acid being broken up to make one of butyric. This fermentation takes place in stagnant liquors, the organism growing in the absence of air, using combined instead of free O. The gallic fermentation attacks the tannin itself, and in the case of some kinds of liquors destroys it very rapidly. The agent of this fermentation is a mould. The growth of a gram of mould involves the destruction of 1,000 grams of tannin and only 0.5 gram of oxygen is used in the process. Once a vat has been invaded by the fungus, it is useless to add fresh tannin, for this at once becomes the prey of the parasite. The chief danger is from the spores which float in the air, and which grow best at 20° C. (68° F.). Formaldehyde and formic acid are useful in preventing the growth of this mould. The author suggests the possibility that antiseptics may be discovered which will permit the growth of beneficial microörganisms and suppress those which are harmful.

Plumping of hides may be brought about by water, and by acids, bases and salts. Water acts in three ways on animal and vegetable tissues:—(*a*) By capillary absorption. The water occupies the spaces previously occupied by air, as in the case of sponge or a lump of sugar; or it increases the distance between the particles, as in the case of clay or hide fiber. (*b*) By osmotic absorption. In this case the phenomenon is due to the presence of a permeable membrane, which permits liquids to pass more easily than matters held in solution. Water penetrates the tissues, while the colloidal materials contained within the tissues cannot escape. This process goes on until the internal pressure equals the exterior osmotic pressure. The final volume is the sum of the original volume plus that of the water absorbed. (*c*) By molecular absorption. In this case the total volume is less than the sum just mentioned. Chemistry affords many examples of this (*e. g.* alcohol and water) and in such cases the contraction of volume is accompanied by rise of temperature. In consequence of the motion of the molecules of a solid, other molecules are able to penetrate between them, and thus the molecules of water are able to get between the molecules of the hide fiber and so permit the entrance of the tannin, which by combining chemically with these molecules forms leather.

Study of these phenomena seems to have established the following principles:—(*a*) Swelling depends partly on the physical and partly on the chemical properties of the body swelled and of the liquid; (*b*) Swelling progresses regularly from the outside to the inside; (*c*) It is accompanied by a contraction of the total volume, (*i.e.*, the volume of the swelled body is less than the sum of its previous volume and the volume of water absorbed); (*d*) Heat is developed. Plumping is less at higher temperatures, and is increased by pressure.

The action of acids used for plumping and of the alkalies during

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unhairing, may be considered from several points of view. Osmotic absorption may be considerably aided by osmotic pressure due to the exterior solution, these bodies being for the most part electrolytically dissociated by water. Most of the substances which produce swelling, on being dissolved in water, develop considerable quantities of heat, which seems to point to the formation of hydrated compounds easily decomposed by further dilution. The water set free under these conditions is especially active in producing hydrolyzation, witness the effect of dilute acids in hydrolyzing starchy bodies. This water may be fixed not only physically, on the glutin of the fibers, but also chemically, making perhaps hydrates of glutin which combine more rapidly with tannin; or causing depolymerization, conducing to the same result. The industrial uses of cellulose furnish a striking example of this kind of chemical transformation.

The phenomena may be more complex, for the glutin of the fibers has in its molecule both the amino group and the carboxyl group, permitting the fixation of both acids and alkalies to form new compounds; less insoluble, more dialyzable and able more easily to enter into reaction.

The essential things in the vats are tannin and acid. The tannin fixes the swelling and so prevents the hide from contracting as it is carried into liquors containing less and less acid. On the other hand, the acid opposes the shrinkage which the astringents tend to produce. The colloids are not alone in their tendency to cause shrinkage; with them belong liquids which dialyze with difficulty, some mineral matters, and even acids when their concentration is high.

Acids, whether added to the liquors or naturally produced in them, have two uses, deliming and plumping. In the case of natural tan-liquors, the acids formed in the liquors delime the hide. The action is rather mild, and the presence of various substances and organisms may do injury to the hides, involving loss of material. It is now generally admitted that baths of lactic, formic or boric acid are on the whole better. The necessary plumping effect is brought about by the natural liquors when they are sound and well managed. The process is slow, and some hide substance is lost in these baths. The acidity of the liquors is liable to be destroyed by injurious organisms. Modern practice frequently reinforces the vat liquors both with acid and tanning extracts. The acids used are largely lactic and formic. The latter is especially valuable because of its antiseptic power.

Tannage is really a chemical phenomenon, accompanied by certain physical processes of less importance, such as absorption, solution, etc. When a solution of gelatine, that is, hydrated glutin, is added to a tannic solution, the precipitation of gelatine tannate is immediate. Hide-powder quickly detannizes a solution of tannin. Why, then, is the industrial tanning process so slow? The answer to this question is very simple. When one wishes a chemical reaction to take place quickly, the substances which are to react are brought into solution or powdered and we use heat, electricity, etc., to hasten the process. It is manifestly im-

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possible to do these things in the tannery. Three methods which have been employed with some success in hastening the tanning process are (*a*) Starting the hides in an excessively swollen condition, thus enabling the tannin to penetrate rapidly. (*b*) The use of pressure, to force the tannin into contact with the fiber. (*c*) Electricity, variously applied.

L. B.

PATENT.

Machine for Fleshing, Unhairing and Working Out Hides and Skins. U. S. Patent No. 999,540. GEORGE W. BAKER, Wilmington, Del.

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Journal of the

American Leather Chemists Association

Vol. VI OCTOBER, 1911 No. 10

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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EIGHTH ANNUAL MEETING.

The 8th annual convention of the A. L. C. A. will be held at Washington, D. C., December 7, 8 and 9, 1911.

H. C. REED, *Secretary.*

OUTLINE OF THE WORK PLANNED BY THE COMMITTEE ON DISPOSAL OF TANNERY WASTE.

By J. H. Russell, Chairman.

In accordance with the newer policy of the A. L. C. A. to

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take up some of the broader problems of the leather industry, there was organized this year a committee on Tannery Waste. That the subject is interesting to the chemists is shown by the fact that, under the new system of choosing committees, twelve members signified their wish to serve on this one. These members are Messrs. W. K. Alsop, I. C. Bull, H. L. Clough (who afterwards withdrew), P. A. Esten, F. M. Loveland, T. J. Mosser, Dr. Allen Rogers, C. C. Smoot, III, W. H. Teas, F. P. Veitch, H. T. Wilson and J. H. Russell, Chairman

It was realized at the start that the work could not be carried on as is the ordinary collaborative work of the association. There could be no series of experiments from the collected results of which it could be hoped to work out a method for the disposal of tannery waste applicable at all tanneries. The problem is in part one of engineering, and so far as the greater number of tanneries in this country are concerned, is a problem of the future. But the basis of the matter is chemical and already the need of solving the problem has arisen in many cases, some of them quite unpleasant for the tanner.

In order to adapt the work to the facilities and interest of the different members of the committee it was decided to divide it into several related parts and to have each member choose the part of the problem on which he wished to work with the hope that all of them would combine in furnishing data and descriptions of a general nature. What does tannery waste consist of in different tannages and how much is there of it? How far do natural agencies go towards purifying it? What methods have been used to purify it artificially and how far have they been successful as to efficiency and cost? In purifying tannery waste is there a possibility of recovering by-products of sufficient value to help pay for the cost of purification? In connection with the nature of tannery waste it is desired to get reports from as many tanneries as possible concerning the nature and amount of waste from each department and of the mixed effluent from the whole tannery. The natural purification of waste is to be studied by the analysis of samples of tannery stream water taken above the tanneries and at various distances and places in the streams below them to note the effect of dilution, oxidation and the precipitating bases natural to the water. Descriptions are desired of present

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methods of purification with tests of their efficiency by analysis of effluent before and after treatment, and, where possible the cost of installing and running the plants. Where methods of sedimentation are used, it is desired to learn the true fertilizer value of this sediment and whether it might pay to dry it out and prepare it for shipment. Mr. Veitch of the U. S. Dept. of Agriculture is making these determinations on such samples of settlings as are sent to him.

In none of the reports is it intended to give the names or locations of any of the tanneries. These have no immediate bearing on the problem and might cause inconvenience. It is the data and descriptions which are of importance.

To aid those who are interested in or working on the subject of tannery waste to become familiar with the work which has already been done on the subject, a bibliography is necessary. This has been prepared by Mr. Esten and is published in this number of the JOURNAL.

Work of the nature outlined above does not fit in at all with the routine work of a laboratory. It must all be done in addition to the regular work and some of it requires the covering of a considerable territory. It will take some time to get together enough results to be valuable for compilation, while the ultimate solution of the problem of tannery waste is probably many years distant. In the mean time most of the members are doing what they can, and from time to time it will be possible to report progress. Dr. Rogers, during the coming year, at Pratt Institute will undertake an important work on Depilation for the National Association of Tanners. In connection with this work he will be able to make careful study of beam house waste and will publish the result of his work along this line. Mr. Alsop has already succeeded in getting a valuable article, "The Treatment of Tannery Effluents," by J. A. S. Morrison for our Journal (July 1911, pp. 326-342) and may be able to obtain other articles on the same subject.

It is hoped that the tanners and chemists generally will coöperate in the work of this committee, because, although the problem may be a pressing one in only a few localities in this country to-day, it is bound to become more important each year. Therefore all the data we can gather now and the studies we can

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make of present methods of disposal and their failures and successes will help tremendously when the problem of tannery waste becomes of general importance to the Leather Industry.

BIBLIOGRAPHY OF TANNERY WASTE TREATMENT.

By P. A. Esten.

There is no very extensive literature on the subject of Tannery Waste. Such as there is, consists, partly, of investigations of individual tanneries by boards of health, and, largely of references to the subject in standard works on the disposal of trades wastes in general. In fact the development of the disposal of tannery waste is so closely connected with that of general sewage disposal that a bibliography, in order to be of value to those wishing to investigate the subject, must make reference to works which mark a distinct advance in the matter of trades wastes in general even if they do not refer specifically to tannery waste. Such works of general importance, but not referring especially to tannery waste are designated "g" in the following bibliography. Some of the references are to reports or journals not readily available. Where these have appeared in condensed form in our own or some other available journal a separate reference marked "c," is made or where abstracts have been made the reference to these is marked "a." The references go back only to the year 1895 as work done previous to that has been largely superseded by later work or is summarized in some of the later references.

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NOTE ON THE ANALYSIS OF TANNINS.

By Louis E. Levi and August C. Orthmann.

In 1889 M. von Gallois was granted a patent (German Patent No. 45,998) for the use of chromium compounds as mordants for textiles. The chromium compounds were the chromium chromate $Cr_2(CrO_4)_3$ and the basic sulpho-chromate $Cr_2SO_4CrO_4(OH)_2$. The theory for the use of these compounds as mordants was—in impregnating the textile the chrome compound would be absorbed, which on subsequent steaming would deposit a precipitate of $Cr_2(OH)_6$ upon the fiber and thereby act as a mordant for the different dyestuffs to be used. As these chrome compounds are easily decomposed in contact with organic materials, the idea was advanced to try these and different chromium compounds for the quantitative determination of tannins. With the theory in mind that the complex chromium com-

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pounds break up into insoluble basic chromium products and precipitate quantitatively according to the amount of tannins present, the method was tried. This indeed seems to be the case with certain chromium compounds, which will be shown as follows, in this, our preliminary note:—

Reagent No. 1. $\underset{206}{Cr_2(OH)_6} + \underset{100}{CrO_3} = \underset{288}{Cr_2CrO_4(OH)_4} +$ H_2O. This proved to be a failure. The given amount of CrO_3 would not dissolve the given amount of $Cr_2(OH)_6$ on account of the excess amount of water present.

Reagent No. 2. $\underset{206}{Cr_2(OH)_6} + \underset{200}{2CrO_3} = \underset{254}{Cr_2(CrO_4)_2(OH)_2}$ $+ 2H_2O$. This met the same fate as reagent No. 1 probably on account of the large amount of water in the $Cr_2(OH)_6$, solution could not be brought about with the aid of heat, although the solution is possible, but on dilution $Cr_2(OH)_6$ would be precipitated.

Reagent No. 3. $\underset{206}{Cr_2(OH)_6} + \underset{300}{3CrO_3} = \underset{452}{Cr_2(CrO_4)_3} + 3H_2O$.

This reagent precipitated the tannins (most common) and also tannic acid, a few quantitative determinations were made but results showed that non-tannin was precipitated with tannic acid.

Reagent No. 4. $\underset{392}{Cr_2(SO_4)_3} + \underset{194}{K_2CrO_4} = \underset{412}{Cr_2CrO_4(SO_4)_2} +$ K_2SO_4.

Reagent No. 5. $Cr_2(SO_4)_3 + 2K_2CrO_4 = Cr_2(CrO_4)_2SO_4 + 2K_2SO_4$.

Reagents Nos. 4 and 5, both precipitated gallic acid, and non-tannins that were not absorbed by hide powder. Although reagent No. 4 precipitated tannic acid quantitatively as shown by the following results. 41.2 gram of the reagent were diluted to 1,000 cc. Ten cc. of this solution was mixed with 10 cc. of 1 per cent. strength tannic acid solution and allowed to stand one-half hour, filtered and washed with cold water, the precipitate was dried, ashed, and fused with $Na_2CO_3 + KClO_3$ and Cr_2O_3 determined by adding H_2SO_4 and KI and titrating with thiosulphate.

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1	=	0.0275884 gm.	Cr_2O_3
2	=	0.0277536 "	"
3	=	0.0275884 "	"
4	=	0.0271754 "	"
5	=	0.0267624 "	"
6	=	0.0270102 "	"
7	=	0.0270102 "	"
8	=	0.0265146 "	"
9	=	0.0270928 "	"
10	=	0.0275058 "	"
11	=	0.0275884 "	"
12	=	0.0275058 "	"

Later we found that the slight error in Cr_2O_3 was due to the fusion mixture used, etc.

Reagent No. 6. $Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$

$Cr_2(SO_4)_2(OH)_2 + K_2CrO_4 = Cr_2SO_4(OH)_2CrO_4 + K_2SO_4.$

This reagent precipitated gallic acid and tannic acid very readily. Lactic acid was added to the tannic acid and gallic acid solutions: on the addition of the reagent no precipitate was formed. The reagent was boiled and then cooled, but this did not prevent the gallic acid from being precipitated. No quantitative determinations were made.

Reagent No. 7. $Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$

$Cr_2(SO_4)_2(OH)_2 + 2K_2CrO_4 = Cr_2(CrO_4)_2(OH)_2 + K_2SO_4.$

This reagent is the same as reagent No. 2 except that it is made with basic chromium sulphate and potassium chromate instead of chromium hydroxide and chromic acid. On boiling, in dilute solution $Cr_2(OH)_6$ was precipitated.

Reagent No. 8. $Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$

$Cr_2(SO_4)_2(OH)_2 + CrO_3 = Cr_2(SO_4)_2CrO_4 + H_2O.$

With this reagent all the tannins were precipitated, and quantitative analyses were made. Eighty-two and four-tenths grams were diluted to 3,750 cc. with distilled water. Twenty cc. of this solution were added to 10 cc. of a 1 per cent. strength tannic

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acid solution the whole diluted to about 100 cc. and boiled for 10 minutes, filtered and washed with hot water, the precipitate analyzed for Cr_2O_3 and the following results were obtained:

1	=	0.07313025 gm.	Cr_2O_3
2	=	0.06532275 "	"
3	=	0.06532275 "	"
4	=	0.06532275 "	"
5	=	0.07963650 "	"
6	=	0.05881650 "	"
7	=	0.06011775 "	"
8	=	0.05881650 "	"
9	=	0.06272025 "	"
10	=	0.05231125 "	"

Later we found that the difference in these results was due to boiling. The following results were obtained by precipitating the same amount of tannic acid with 20 cc. of reagent No. 8 and allowing the mixture to stand 15 hours (over night) without boiling.

1	=	0.06824841 gm.	Cr_2O_3 in precipitate
2	=	0.06824841 "	" " " "
3	=	0.06550751 "	" " " "
4	=	0.06687796 "	" " " "
5	=	0.06687796 "	" " " "

This reagent is still under consideration and later we expect to make analysis of the tannins with it. At this point we also had considerable trouble finding a perfect fusing mixture, $Na_2CO_3 + KClO_3$ would sputter over the crucible unless very carefully watched, a hot flame could not be applied. Then we tried $Na_2CO_3 + K_2CO_3 + KNO_3$ in different proportions, with the same results, beside sputtering the different fusion mixtures would creep over the top to the outside of the crucible. We also tried Na_2O_2 in an iron crucible but this required another filtration and another chance of error. Finally we found that a mixture of borax glass and sodium and potassium carbonates answered the purpose nicely.

The filtrate was oxidized with Na_2O_2 and boiled until the excess of Na_2O_2 was decomposed and all oxygen boiled off and the process carried out as usual, this gave just as good results as the direct method, *i.e.*, fusing the precipitate.

Reagent No. 9. $Cr_2(SO_4)_3 + 3K_2CrO_4 = Cr_2(CrO_4)_3 + 3K_2SO_4$?

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This reagent is the same as No. 3 but made from different reagents. Quantitative determinations were made, 22.6 grams of the compound were diluted to 500 cc., 10 cc. of this were added to 10 cc. of a 1 per cent. solution of tannic acid, this was diluted to about 100 cc. and allowed to stand one-half hour filtered and washed, the precipitate was fused and Cr_2O_3 determined as usual.

1	=	0.0603146	gm. Cr_2O_3	
2	=	0.0609360	" "	
3	=	0.0646670	" "	This precipitate was not washed enough.
4	=	0.0600037	" "	
5	=	0.0606255	" "	
6	=	0.0606255	" "	
7	=	0.0603146	" "	
8	=	0.0618691	" "	
9	=	0.0609360	" "	

The reagent also precipitated the tannins but had to be rejected on account of precipitating non-tannins and gallic acid.

Reagent No. 10. $2Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_4(SO_4)_5(OH)_2 + Na_2SO_4 + CO_2.$

$Cr_4(SO_4)_5(OH)_2 + K_2CrO_4 = Cr_4(SO_4)_4(OH)_2CrO_4 + K_2SO_4.$

Thirty-eight and seven-tenths grams were diluted to 1,000 cc. Tannic acid was precipitated very slowly, gallic acid still slower, on addition of lactic acid no precipitate was formed. The reagent was boiled and qualitative tests were made but this did no good.

Then qualitative tests were made by boiling the mixture of the reagent and tannic acid, the precipitate formed immediately. Gallic acid also formed a precipitate in hot solution. Tests showed that the precipitation of tannic acid was not quantitative.

Reagent No. 11. $2Cr_2(SO_4)_3 + K_2CrO_4 = Cr_4(SO_4)_5CrO_4 + K_2SO_4.$

This reagent precipitated tannic acid very slowly.

Rejected on account precipitating non-tannins and gallic acid.

Reagent No. 13. $2Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_4(SO_4)_5(OH)_2 + Na_2SO_4 + CO_2.$

$Al_4(SO_4)_5(OH)_2 + K_2CrO_4 = Al_4(SO_4)_4(OH)_2CrO_4 + K_2SO_4.$

This reagent proved to be a failure, when K_2CrO_4 was added to the basic aluminum sulphate a precipitate was formed, hence

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this was rejected. Pure alum was used in place of aluminum sulphate with the same result.

Reagent No. 14. $Al_2(SO_4)_3 + K_2CrO_4 = Al_2(SO_4)_2CrO_4 + K_2SO_4$.

This reagent was as disappointing as reagent No. 13.

Reagent No. 15. $2C_9H_7N : C_3H_6O_3 + Cr_2(CrO_4)_3 =$ reagent.

This reagent was made by adding 258 grams chinolin to 180 grams of lactic acid, and adding 452 grams $Cr_2(CrO_4)_3$ (Reagent No. 9). It precipitated both gallic and tannic acid. Rejected. On standing, the CrO_4 in the reagent was reduced.

Reagent No. 16. $2C_9H_7N : C_3H_6O_3 + Cr_2CrO_4(SO_4)_2 =$ reagent.

This reagent precipitated tannic and gallic acid very slowly. On standing the same change took place as in reagent No. 15.

Reagent No. 17. $4C_9H_7N : C_3H_6O_3 + Cr_4(SO_4)_5CrO_4 =$ reagent.

This reagent precipitated the tannins, but not quantitatively. Like Nos. 15 and 16 it was rejected because it was not stable.

Reagent No. 18. $4C_9H_7N.C_3H_6O_3 + Cr_4(SO_4)_4(OH)_2CrO_4 =$ reagent.

Reagent No. 19. $2C_9H_7N.C_3H_6O_3 + Cr_2SO_4(OH)_2CrO_4 =$ reagent.

Both Nos. 18 and 19 were rejected because they were unstable.

Reagent No. 20. $2C_9H_7N + H_2SO_4 = (C_9H_7N)_2.H_2SO_4$

$(C_9H_7N)_2.H_2SO_4 + Cr_2(SO_4)_3.K_2SO_4 =$ reagent.

This reagent precipitated the tannins and produced a slight precipitate with gallic acid. Examination of the precipitate showed that no chrome compound was formed. Rejected.

Reagent No. 21. $2C_9H_7N + 2C_7H_6O_3 + Cr_2CrO_4SO_4(OH)_2 =$ reagent.

Salicylic acid was not soluble in chinolin and $Cr_2CrO_4SO_4(OH)_2$.

Reagent No. 22. $2(C_5H_5N + C_3H_6O_3) + Cr_2CrO_4SO_4(OH)_2 =$ reagent.

This reagent precipitated tannin acid and also gallic acid: CrO_4 was reduced, rejected.

Reagent No. 23. $4C_5H_5N + C_3H_6O_3 + Cr_4(SO_4)_4(OH)_2CrO_4 =$ reagent.

This reagent precipitated tannic acid, but not gallic acid. Tests showed that it was not quantitative.

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Reagent No. 24. $2Cr_2(SO_4)_3 + Na_2CO_3 + H_2O =$
$Cr_4(SO_4)_5(OH)_2 + Na_2SO_4 + CO_2.$
$Cr_4(SO_4)_5(OH)_2 + CrO_3$
$= Cr_4(SO_4)_5CrO_4 + H_2O.$

After diluting the reagent and boiling, qualitative tests were made. A precipitate was formed with tannic acid but this was slight and very slow. Gallic acid produced a very small precipitate after standing about 15 hours, rejected.

Reagent No. 25 same as No. 24.

Reagent No. 26. $Cr_2Cl_6 + Na_2CO_3 + H_2O$
$= Cr_2Cl_4(OH)_2 + 2NaCl + CO_2.$
$Cr_2Cl_4(OH)_2 + CrO_3 = Cr_2Cl_4CrO_4 + H_2O.$

This is the same as reagent No. 8, Cr_2Cl_6 was used instead of $Cr_2(SO_4)_3$, no precipitate was formed with tannic nor gallic acid, rejected.

Reagent No. 27. $Cr_2Cl_6 + K_2CrO_4 = CrCl_4CrO_4 + 2KCl$?

Results were the same as with No. 26.

Reagent No. 28. $Cr_2(SO_4)_3 + Na_2CO_3 + H_2O$
$= Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$
$Cr_2(SO_4)_2(OH)_2 + 2CH_3COOH$
$= Cr_2(SO_4)_2(C_2H_3O_2)_2 + H_2O.$
$Cr_2(SO_4)_2(C_2H_3O_2)_2 + Na_2CO_3 + H_2O$
$= Cr_2SO_4(C_2H_3O_2)_2(OH)_2$ etc.
$Cr_2SO_4(C_2H_3O_2)_2(OH)_2 + CrO_3$
$= Cr_2SO_4(C_2H_3O_2)_2CrO_4 + H_2O.$

This reagent did not precipitate tannic acid nor gallic acid in cold solution, but on boiling a heavy precipitate with tannic acid and a light precipitate with gallic acid was formed.

Reagent No. 28a. This was made in the same way as No. 28 substituting chrome alum for chromium sulphate. Results were the same as above. Rejected on account of precipitating gallic acid.

Reagent No. 29. $Cr_2(SO_4)_2(C_2H_3O_2)_2 + K_2CrO_4$
$= Cr_2SO_4(C_2H_3O_2)_2CrO_4$, etc.

This reagent was made from $Cr_2(SO_4)_3$. In the cold solution no precipitate was formed with tannic nor gallic acids, on

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boiling and standing for an hour, a light precipitate was formed with tannic acid, but none with gallic acid.

Reagent No. 29a. $Cr_2(SO_4)_2(C_2H_3O_2)_2 + K_2CrO_4 = Cr_2SO_4(C_2H_3O_2)_2CrO_4$, etc.

This reagent was made from chrome alum.

In the cold solution a precipitate was formed with gallic and tannic acid after long standing. On boiling, a large precipitate was quickly formed.

Reagent No. 30. $Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2$, etc

$$Cr_2(SO_4)_2(OH)_2 + Ba(C_2H_3O_2)_2 = Cr_2SO_4(C_2H_3O_2)_2(OH)_2, \text{ etc.}$$

$$Cr_2SO_4(C_2H_3O_2)_2(OH)_2 + CrO_3 = Cr_2SO_4(C_2H_3O_2)_2CrO_4, \text{ etc.}$$

Chrome alum was used to make this compound, enough $Ba(C_2H_2O_2)_2$ was added to allow for the extra SO_4 in the chrome alum. The $Ba(C_2H_3O_2)_2$ was added to the boiling solution and the $BaSO_4$ was filtered off, then the CrO_3 was added and the whole boiled, and cooled before using. This reagent produced a precipitate with tannic acid and the tannins, also a small precipitate with gallic acid.

Quantitative determinations were made with tannic acid, but the reagent was rejected on account of precipitating gallic acid and non-tannins.

Reagent No. 31. $Cr_2(SO_4)_3 + Ba(C_2H_3O_2)_2 = Cr_2(SO_4)_2(C_2H_3O_2)_2$, etc.

$$Cr_2(SO_4)_2(C_2H_3O_2)_2 + K_2SO_4 = Cr_2SO_4(C_2H_3O_2)_2CrO_4, \text{ etc.}$$

Chrome alum was used here also, and made the same way as No. 30 using K_2CrO_4 instead of CrO_3 and $Cr_2(SO_4)_2(C_2H_3O_2)_2$ instead of $Cr_2SO_4(C_2H_3O_2)_2(OH)_2$.

This reagent precipitated the tannins and produced a small precipitate with gallic acid. So far we have made no quantitative determinations but the reagent is still under consideration.

Reagent No. 32. $Cr_2(OH)_6 + 2H_2SO_4 = Cr_2(SO_4)_2(OH)_2$, etc.

$$Cr_2(SO_4)_2(OH)_2 + CrO_3 = Cr_2(SO_4)_2CrO_4, \text{ etc.}$$

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This is the same as No. 8, using $Cr_2(OH)_6$ instead of $Cr_2(SO_4)_3$. All the tannins were precipitated with this reagent: gallic acid showed no precipitate.

Quantitative tests were made with tannic acid. The portions taken were the same as before mentioned. Results

1	=	0.06961886 gm.	Cr_2O_3	in	precipitate
2	=	0.06961886 "	"	"	"
3	=	0.07235976 "	"	"	"
4	=	"	"	"	"
5	=	"	"	"	"

The reagent is still under consideration and we hope to produce some good results with same.

Reagent No. 33. $Cr_2(OH)_6 + 2H_2SO_4 = Cr_2(SO_4)_2(OH)_2$, etc.

$Cr_2(SO_4)_2(OH)_2 + Ba(C_2H_3O_2)_2 = Cr_2SO_4(C_2H_3O_2)_2(OH)_2$, etc.

$Cr_2SO_4(C_2H_3O_2)_2(OH)_2 + CrO_3 = Cr_2SO_4(C_2H_3O_2)_2CrO_4$, etc.

The $Cr_2(OH)_6$ was freshly precipitated and washed free from sulphate and chlorides, the H_2SO_4 was added and heated until all $Cr_2(OH)_6$ was dissolved, then to the boiling solution $Ba(C_2H_3O_2)_2$ was added, after boiling five minutes this was allowed to stand over night and then filtered and the $BaSO_4$ washed free from chrome. To the filtrate CrO_3 was added and the solution was again boiled, then it was allowed to cool.

This reagent precipitated all the tannins, tannic acid and not non-tannins, from the hide powder method.

It will be noticed that reagents Nos. 28, 28a, 29, 29a, 30 and 31 are all the same compound made in as many different ways.

Having at last found a reagent that would precipitate the tannins quantitatively and not precipitate the non-tannins we started the determinations of the different tannins with the reagent No. 33. ($Cr_2SO_4(C_2H_3O_2)_2CrO_4$).

Our first problem was to obtain a factor with pure tannic acid, the factor alone was easy to obtain but to obtain tannic acid that was absolutely pure from gallic acid was a difficult matter.

We spent several weeks on this. We soon found that tannic acid free from gallic acid could not be obtained from the differ-

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ent chemical houses, so the only thing left for us to do was to make it.

The method we finally adopted to purify tannic acid was, washing a fairly pure product with absolute ether. The tannic acid (about 15 grams) was shaken with ether (75 to 100 cc.) three or four times, then the ether poured off and fresh ether added, this was repeated from 15 to 20 times and the result was tannic acid that showed no gallic acid by testing with a solution of pure KCN. The ether was evaporated off, and the tannic acid was dried at 110° C. for two hours, placed in a clean; well stoppered bottle in a desiccator until we were ready to use it.

We tried other methods for the purification of tannic acid but found the above method best suited to our purpose.

The following is the method we used to get our factor for tannic acid. All precipitations being in the cold. 43.4 grams or $Cr_2SO_4(C_2H_3O_2)_2CrO_4$ were diluted to 2,000 cc. Five grams of pure tannic acid were dissolved in 500 cc. water. Twenty cc of the reagent were added to 10 cc. of the tannic acid solution. The mixture was allowed to stand 15 hours (over night), to complete the reaction that takes place. Twelve hours standing is necessary. Then filtered and washed with cold water until the precipitate is free from the excess of reagent. The Cr_2O_3 was determined by the direct method (the Cr_2O_3 in the precipitate) and by the indirect method (determination of Cr_2O_3 in unused portion of reagent in the filtrate). Cr_2O_3 was determined by the iodometric method.

Following are the results for tannic acid factor.

0.1 gram tannic acid was used.

	Direct method			Indirect method		
1 =	0.0659276	gm.	Cr_2O_3	0.0663729	gm.	Cr_2O_3
2 =	0.0659276	"	"	"	"	"
3 =	0.0663729	"	"	"	"	"
4 =	"	"	"	"	"	"
5 =	"	"	"	"	"	"
6 =	"	"	"	"	"	"
7 =	"	"	"	"	"	"
8 =	"	"	"	"	"	"
9 =	"	"	"	"	"	"
10 =	"	"	"	"	"	"

The precipitate formed with 0.1 gram tannic acid contained

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0.0663729 gram Cr_2O_3 and this calculated to the hypothetical monoglucoside $C_{20}H_{20}O_{14}$ gave us a factor of 0.0441571 gram Cr_2O_3, which is used in our work.

The following are comparisons. Hide powder method and our new method. Reagent No. 33.

	Hide powder method Per cent. tannin	New method Per cent. tannin
Liquid quebracho extract	33.63	34.84
Chestnut oak extract liquid	25.04	26.08
Sumac extract liquid	22.23	27.29
English liquid quebracho extract	37.92	39.97
Hemlock extract liquid	27.25	23.19
Italian chestnut extract	32.25	36.14
English liquid myrobalans extract	33.26	31.59
Quermos extract liquid	37.09	42.04
Ordinary layer extract liquid	33.80	31.26
Special layer extract liquid	31.69	28.08
Liquid quebracho extract S. M	36.61	36.55

The above comparative analyses were all made in triplicate. We are continuing our experiments on these lines and hope in the near future to publish the complete results of all our experiments and at the same time give the leather chemists a new, quick and accurate method for the analysis of liquors, tannins, etc. We are also experimenting with aluminum chrome and chrome organic aluminium organic and aluminium chrome organic compounds. The determination of the non-tannins will also be published in the near future.

THE TANNINS.

Characteristic Reactions of Value for their Identification and Detection in Mixtures.

By A. W. Hoppenstedt.

With the passing of the days of tanning leather with a single tanning material and the advent of mixed tannages and the use of extracts, new conditions have been created which demand of the leather chemist the ability to detect and determine the constituent tanning materials of a product. The present state of our knowledge, the lack of reliable tests for the identification

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of the different tannins, and the complex, undefined and scattered condition of the literature on the subject, have long been a source of worry to leather chemists. These conditions have led the author to attempt to compile, arrange and establish in a concise, clear and defined way, all such tests which are of real value to the investigator. The work was started by gathering and investigating all tests published on the subject, discarding the worthless ones and retaining and establishing on a satisfactory basis all those of actual value. Therefore all tests given in the following compilations have been thoroughly examined in the author's laboratory and their value and reliability proven, and no tests are quoted that were found valueless or of such a nature that their application would yield no information of value. Furthermore only the qualitative side of the question has been approached without any consideration of quantitative reactions, and not all of the known tanning materials have been subjected, but mainly those used in this country, though in time all materials of any significance will be included. At the outset, the author desires it to be understood that the strength of all tannin solutions referred to, is analysis strength (Official Method A. L. C. A.) and as made up for analysis, unless otherwise stated.

Part 1. *Cathechol Tannins. General Characteristics. Precipitated by Bromine Water.*

Place in test-tube 2 cc. of the clear filtered tannin solution as obtained under determination of soluble solids and add one small drop of a 5 per cent. solution of acetic acid. Mix thoroughly. Then drop in slowly, with constant agitation, 5 cc. of bromine water containing 4-5 grams of bromine per liter.

H. R. PROCTER, Leather Industries Laboratory Book.

All the catechol tannins give voluminous precipitates with the bromine water except heavily bisulphited quebracho which gives only a slight but sufficient precipitate.

Section A. Green Blacks with Ferric Alum.

Place in test-tube 1 cc. of the clear filtered tannin solution as obtained under determination of soluble solids and add 20 cc.

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of distilled water. Mix thoroughly. Then add 1 cc. of a 1 per cent. solution of ferric ammonium sulphate. Mix again.

H. R. PROCTER, Leather Industries Laboratory Book.

The tannins in this section give a green coloration.

Completely Precipitated by Formaldehyde and Hydrochloric Acid.

Place 50 cc. of the tannin solution in an Erlenmeyer flask and add 10 cc. of formaldehyde (40 per cent.) and 10 cc. of hydrochloric acid prepared by diluting the concentrated acid with equal parts of water. Boil with reflux condenser for 10 minutes, then cool and filter. Place 10 cc. of the clear filtrate in a test-tube, add 2 grams of dry sodium acetate, C. P., and shake until dissolved. Then add slowly from a pipette 5 cc. of a freshly prepared 0.1 per cent. solution of ferric ammonium sulphate allowing the same to carefully run down the side of the tube. Do not mix.

E. STIASNY, *Der Gerber*, 1908, 815, 222.

The tannins in this section give no reaction or only a very faint blue ring at the junction of the liquids. If a pyrogallol tannin is present, an intense blue ring is produced at the junction of the liquids.

Tannins of this Section.

Quebracho.

Mangrove.

Gambier.

Cutch.

Quebracho.

Place 10 cc. of the tannin solution in a test-tube and add 10 cc. of ethyl acetate. Mix thoroughly by shaking and then allow

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layers to separate. The ethyl acetate assumes a strong green color and forms the upper layer.

C. KOERNER, *Collegium*, 1903, 2, 100.

This reaction is given by all grades of quebracho extract both clarified and unclarified and not by any of the other tannins. Amyl acetate also produces the reaction but not quite as strong.

(To be continued)

QUALITATIVE REACTIONS OF VEGETABLE TANNINS.[1]

By Edmund Stiasny and C. D. Wilkinson.

The last Conference of the I. A. L. T. C. in Paris, September, 1910, has decided that the behavior of vegetable tannins against different reagents should be studied by a commission. The following report of our experimental results may be regarded as a first step in this work, and it is published here mainly for the purpose, that our suggestions may be examined by as many colleagues as possible, and that the collected report of a large number of tests carried out by different workers may prove valuable for our knowledge on vegetable tannins.

The goal which we must finally try to reach is, identify a single tannin material in the form of its extract or liquor, to prove decidedly if any extract is pure or not, and to determine the components in any mixtures of vegetable tannin solutions.

Any work in this direction has to be based on our present knowledge of the qualitative behavior of tannins, starting with the examination of these known tests and trying to modify and elaborate them to increase their value. Procter's "Laboratory Book" is the best guide for this part of the work, and we have made use of it in many respects. Another part of our work deals with attempts to find new methods for distinguishing different vegetable tannins. Here we hope to give some valuable suggestions, as well as to state some negative results, in order to prevent other colleagues from wasting time with similar experiments.

No color tests have been used, because they are liable to individual errors, and principally because they do not work in the

[1] *Collegium*, 1911, Nos. 475 and 476, pages 318-332.

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case of mixtures. We thought that those tests were the more important ones, which allow a separation of different tannins; we therefore studied mostly precipitation tests as to the formation, completeness and solubility of the precipitate formed. As a preliminary scheme the following tests and conditions were chosen. The tannin solution was made of three different concentrations, viz., analytical strength (3.5—4.5 gram tannin per liter), one-tenth of this strength, and 6—8 times the same. The observations were made immediately, and when required repeatedly during the first hours, and in all cases after allowing them to stand over night. The reagents were always used in the concentration given below and added to the tan solutions by means of pipettes, so that the most possible conformity may be obtained by different workers.

In this way, 34 different tannin solutions[1] were tested with sodium chloride, ammonium chloride, ammon-acetate, tartar emetic, lead acetate, bromine, copper sulphate and ammonia; ammonium sulphide, and formaldehyde. The results allowed us to eliminate those tests which did not prove to be of value (precipitating with saturated solutions of sodium chlorid, and ammonium chlorid, and testing with ammonium sulphide)[2] and to choose the most suitable tannin concentrations for the other promising tests. It would take up too much space to give these preliminary results in table form and we may at once shortly report on the promising tests and their application for distinguishing some tannins in mixtures.

A. The lead acetate test.

1. *Completeness of the Lead Acetate Precipitation.*

All tannins are completely precipitated in as far as the filtrate from this precipitate gives in no case the iron-test (adding about 1 cc. iron alum solution (1 per cent.) to about 5 cc. of the filtrate). Valonia (2),[3] mimosa (2), mangrove (2), oakwood, chestnut (3), myrobalans (4), algarobilla, divi-divi and

[1] All tanning materials and extracts used in this paper are guaranteed pure materials, kindly sent for our use by several tannin extract works in England and the Continent.

[2] The Eitner-Philip test will be dealt with below.

[3] These figures in brackets mean the number of samples of different extracts which have been tested.

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gallotannic acid give no coloration, if excess of NaOH is added (to redissolve $Pb(OH)_2$) to the filtrate of the lead acetate-precipitate. But quebracho (6 extracts and a pure sample of wood) gives a yellowish color, the intensity of which increases with standing; the same is the case with ulmo, and most distinct with sumach (3 extracts and several samples of pure Sicilian sumach) and pistacia.

As to quebracho, the observation may be made that after shaking out the aqueous solution with ethylacetate, the remaining aqueous layer when precipitated with lead acetate gives a filtrate which remains colorless after addition of NaOH.

Basic lead acetate leads in all cases to a filtrate which remains colorless after adding excess of NaOH.

Some samples of wood pulp (4) are not, others only very incompletely, precipitated with lead acetate and a little more but still always incompletely with basic lead acetate, the filtrate being yellow and giving distinctly deper color with NaOH.

2. *Solubility of the Lead Precipitate in Acetic Acid.*

Quebracho (3), mangrove (2), ulmo, mimosa (2), gambier gave a lead precipitate which was entirely soluble in acetic acid. The test was made by adding 10 cc. acetic acid (10 per cent.) to the mixture of 5 cc. tannin solution and 5 cc. lead acetate (10 per cent.); or, preferably, by first adding 10 cc. acetic acid to 5 cc. of the tannin solution, and then adding 5 cc. of the lead acetate. In the latter case no precipitate is produced with catechol tans, provided they have not been sulphited (3). Then of course some lead sulphate is formed and small amounts of tannin are carried down by this precipitate. The behavior of pistacia is stated later on.

Pyrogallol tans differ from the behavior of catechol tans, their lead precipitate being insoluble or but partially soluble in acetic acid. Insolubility was observed in the case of oakwood, chestnut (some samples showed a small solubility) and valonia, partial solubility in the case of sumach, myrobalans, divi-divi, algarobilla and gallotannic acid.

The following table I shows the behavior of catechol and pyrogallol tans, of wood pulp and some mixtures.

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TABLE I

5 c.c. tannin solution (analytical strength) + 10 c.c. acetic acid (10 per cent.) and 5 c.c. lead acetate (10 per cent).

Catechol tans	Reaction of the filtrate	
	+Iron alum	+Iron alum +Sodium acetate
Quebracho no pp	olive-green	violet
Quebracho sulf. very slight pp	green	violet
Mangrove no pp	olive-green	violet
Ulmo " "	green	violet
Gambier " "	green	deep green, the lower layer clear blue
Mimosa " "	deep bluish violet	deep bluish violet
Pistacia pp	both green and violet	both dirty green and violet
Wood pulp no pp	no distinct coloration	no distinct coloration
Pyrogallol tans		
Chestnut pp	faint bluish violet	violet
Oakwood "	no distinct coloration	no distinct coloration
Valonia "	no distinct coloration	no distinct coloration
Sumach "	violet	violet
Divi-divi "	violet	violet
Algarobilla pp	violet	violet
Myrobalans "	deep bluish violet	deep bluish violet
Gallotannic acid pp	deep bluish violet	deep bluish violet
Mixtures		
Oakwood and quebracho (20%) pp.	faint green	faint violet
Chestnut and quebracho " "	faint dirty green	violet
Valonia and quebracho " "	green	violet
Chestnut and myrob's " "	violet	violet
Oakwood and myrob's " "	faint violet	violet
Valonia and myrob's " "	faint violet	violet

Some remarks may be added to Table I. Mimosa, it is known (see Procter's Laboratory Book, p. 161) behaves differently towards ferric salts than the other catechol tans; this is also observed in the filtrate of the acetic acid lead acetate precipitation, which turns violet and not green after adding the ferric salt. The green color produced in the filtrates of the other catechol tans is best observed during the addition of iron alum (added from a dropping bottle). Subsequent addition of solid sodium acetate turns this green color into a distinct violet; only

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gambier remains green, the shade being intensified by the sodium acetate, and the lower layer near the solid salt appearing bright blue. In the case of pistacia, a copious precipitation is obtained with acetic acid and lead acetate, and in the filtrate both the green and the violet coloration can be distinctly seen after adding the iron salt, showing that pistacia contains a mixture of different tans.

Application of the Lead Acetate Test for the Detection of Mixtures.

(*a*) A test for wood pulp extract suggests itself by the different behavior of wood pulp and tanning liquors towards lead acetate. To 5 cc. tannin solution (analytical strength) 5 cc. lead acetate (10 per cent.) are added, and a portion of the clear filtrate is mixed with an excess of NaOH (10-20 per cent.) (the NaOH solution ought to be fairly fresh); if the filtrate remains colorless, no wood pulp is present; 10-20 per cent. wood pulp extract will give distinct yellow color, but a slight yellow coloration may also be due to the presence of quebracho, sumach and pistacia; in this case the test must be repeated with basic lead acetate, when a yellow coloration of the filtrate by addition of NaOH will be due to wood pulp only. But unfortunately the delicacy of the test with basic lead acetate is much less than that with lead sugar, and smaller amounts of wood pulp easily escape observation. The lead acetate test may be considered valuable in the case of determining wood pulp in chestnut extracts. If the formaldehyde test shows absence of any precipitate during testing and the lead acetate test gives yellow coloration, then the presence of wood pulp is proved.

In all cases, however, it is advisable to apply Procter and Hirst's aniline test to confirm the result. (See *Collegium*, 1909, page 185.)

(*b*) Detection of catechol tans in mixtures with oakwood, chestnut and valonia extracts, 5 cc. tannin solution (analytical strength) + 10 cc. lead acetate (10 per cent.), mixed, filtered, and some drops of iron alum (1 per cent.) added to the filtrate. If a green color appears, which is best observed during the addition of the iron salt from a dropping bottle, the presence of catechol tans is proved. This test, however, is not very delicate,

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showing scarcely less than 10-15 per cent. of the catechol tan, and requiring some practice in its use. (See table I, mixtures.)

(*c*) Even the presence of myrobalans in oakwood, chestnut or valonia can be observed with some degree of reliability by the acetic acid lead acetate test, the filtrates of the precipitates of pure oakwood, chestnut or valonia remaining colorless (or nearly colorless with iron alum while the presence of myrobalans (as well as that divi-divi, algarobilla, and sumach) produces a distinct violet tint. (See table I, mixtures.)

B. The tartar emetic test.

1. Five cc. tannin solution (analytical strength) + 10 cc. tartar emetic (4 per cent.). Quebracho (6), mangrove (2), and ulmo gave no precipitate (in some cases the solution after 24 hours turned turbid); gambier became turbid; chestnut (3), mimosa (2),[1] myrobalans (4), sumach (3), valonia (2), pistacia, divi-divi, and algarobilla gave more or less incomplete precipitates. The filtrate of these precipitates gave green color with iron alum; this is—in the case of pyrogallol tans—due to the presence of tartaric acid. One sample of oakwood was completely precipitated, the filtrate not answering to the iron test. Wood pulp solution is not precipitated by tartar emetic.

It may be specially mentioned that mimosa behaves like a pyrogallol tan in this test; we shall see later on that such behavior of mimosa is met with in several other reactions.

2. Five cc. tannin solution (analytical strength) + 10 cc. of a mixture of tartar emetic (4 per cent.) and sodium chloride (4 per cent.).

All tannins were precipitated, but only in the case of oakwood, the precipitation was complete. Wood pulp is not precipitated by this test.

C. The ammon-acetate test.

This test is best carried cut with strong tannin solutions.

Five cc. tannin solution (6-8 times analytical strength) + 10 cc. ammon-acetate (40 per cent.). All catechol tans (quebracho (6), mangrove (2), ulmo, mimosa (2), gambier, and pistacia) give no precipitate. On the contrary they often become clearer than before. If alumina salts are present, even in very small amounts, a copious precipitate appears. Chestnut and oakwood

[1] One mimosa sample gave precipitate only after standing over night.

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give immediately copious precipitate. Valonia, myrobalans, algarobilla and divi-divi are gradually precipitated, while in the case of sumach a precipitate could only be observed after standing for hours (over night). Wood pulp alone gives no precipitate, but mixtures of wood pulp with any tannin gives immediately copious precipitate.

Application of the Ammon-Acetate Test.

As a negative test for wood pulp in mixture with catechol tans. If no precipitate appears, wood pulp is absent.

D. The copper sulphate-ammonia test (See Procter, Laboratory Book, p. 150.)

This test is best carried out in very dilute tannin solutions.[1] Two or three cc. tannin solution (0.1 analytical strength) + 3 — 5 drops copper sulphate (1 per cent.) + about 3 cc. NH_3 (5 per cent. NH_3).

Quebracho (6), mangrove (2), ulmo, gambier, pistacia give no precipitate. Chestnut, oakwood, sumach give immediately precipitate, mimosa gave precipitate after standing over night; three of the myrobalan extracts which we investigated gave no precipitate, one gave a precipitate after standing over night; algarobilla and divi-divi gave slight precipitates after standing for some time; wood pulp gives no precipitate.

E. The Eitner-Philip Test.

Twenty-five cc. tannin solution (6 times analytical strength) + 2-3 drops concentrated sulphuric acid (in case of sulphited extracts take 4-5 drops; excess of acid must be avoided in order to prevent separation of sulphur on the subsequent addition of ammonium sulphide); boil one to two minutes, cool down, add about 5 grams sodium chloride, mix and allow to stand for 5-10 minutes, filter and make the following test with the filtrate: Take 15 cc. of water in a test-tube, add 10-15 drops of yellow ammonium sulphide and 2-3 cc. of the filtrate, and note the appearance of a precipitate.

Quebracho (6), mangrove (2), ulmo, gambier, gave no precipitate. Mimosa, chestnut, oakwood, myrobalans (4), sumach

[1] Oakwood, chestnut, myrobalans, mimosa gave no precipitate in solutions of analytical strength or in still stronger solutions; but they gave positive tests in 0.1 analytical strength.

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(3), divi-divi, algarobilla and pistacia give precipitate. Some wood pulp extracts gave a precipitate, others did not.

Our observations agree entirely with those of Philip (*Coll.*, 1909, p. 249) mimosa behaves here also like a pyrogallol tan; the same may be said of pistacia.

F. The formaldehyde.

Fifty cc. tannin solution (analytical strength) + 5 cc. strong hydrochloric acid + 10 cc. Formaldehyde (40 per cent)[1] boiled with reflux condenser for half an hour, cooled down very well and filtered. The appearance of a precipitate whilst boiling has to be looked for, and the filtrate is used for the following two tests:

(A) Put about 10 cc. of the filtrate in a test-tube and add about 1 cc. iron alum (1 per cent) + about 5 grams, sodium acetate (solid) (not shaking); observe if blue (or violet) color appears in the lower layer.

(B) About 5 cc. filtrate + excess of NaOH (made alkaline); observe if coloration appears.

Table II contains the results obtained by the above tests; similar observations have been published by one of us in *Der Gerber*, 1905.

TABLE II.

	Behavior during 10 15 min. boiling	Color of filtrate	Reaction of the filtrate: + iron alum + sodium acetate	Reaction of the filtrate: + NaOH
Quebracho (7) ..	pp	colorless	not blue	slightly yellow, color increasing by standing
Mangrove (3) ...	pp	"	"	
Ulmo.....	pp	"	"	
Mimosa	pp	"	"	colorless
Gambier.....	pp	"	"	slightly yellow
Pistacia	pp	"	blue	reddish brown
Oakwood.....	clear	slightly colored	"	" "
Chestnut (3)....	clear	" "	"	" "
Myrobalans (4).	clear to turbid	" "	"	" "
Valonia (2).....	clear to turbid	" "	"	" "
Sumach (3)	gradual pp	distinctly "	"	" "
Divi-divi	clear to turbid	strongly "	"	yellow to red to yellow (again)
Algarobilla	clear to slightly turbid	" "	"	red
Wood pulp (4).	clear	dark	not blue	very dark

[1] We took usually 50 cc. of the tanning liquor and added 25 cc. of a solution containing 100 cc. strong HCl, 100 cc. water and 150 cc. Formaldehyde (40%).

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This table shows, that catechol tans are completely precipitated in as far as no iron test is given by the filtrate; but only in the case of mimosa no coloration was produced with excess of NaOH: this of course makes it impossible to suggest a method of detecting wood pulp in mixtures with catechol tans (only in mixtures with mimosa this test could have such application). Pistacia does not behave as a pure catechol tan according to the formaldehyde test.

No pyrogallol tan is completely precipitated, most of them giving no or only very slight precipitate; sumach gives by far the most precipitate, especially after cooling, so that the difference between sumach and pistacia is very small indeed as far as the formaldehyde is concerned.

The iron test is the most useful for testing the filtrate of those precipitates, especially if a mixture of catechol or pyrogallol tans is given, in which case amounts of 5 per cent. pyrogallol tan (and even less) can be detected with accuracy. The frequent adulteration of catechol tannin extracts with myrobalans can thus very easily be found. Wood pulp behaves like pyrogallol tans but no iron test is given.

G. The bromine test. (See Procter, Laboratory Book, p. 149.)

Two or three cc. tannin solution (analytical strength) + 5-10 drops bromine water containing 4-5 grams bromine per liter.

As is generally known, catechol tans give a precipitate while pyrogallol tans do not. The delicacy of the test is very different with different catechol tans, and we have also found that presence of wood pulp prevents (or if present in smaller quantities diminishes) the precipitation. This is the case even if a considerable excess of bromine is used, and can therefore not be due to the presence of sulphites. We have also observed that the precipitate formed by catechol tans with bromine is redissolved by adding wood pulp solution.

H. Solubility tests.

It was suggested by Prof. Procter to determine the solubility of the different tannins in organic solvents by either shaking out the aqueous tannin solutions with a solvent, not miscible with water, or to precipitate the aqueous tannin solution by adding a solvent miscible with water. Both ways have been tried and proved very promising.

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It must be mentioned that Hinrichsen and Kedesdy in their investigation of inks have determined the solubility of some tanning agents in ethylacetate. Their results were so encouraging, that we decided to start this part of our work by

1. Shaking out the aqueous solutions with ethylacetate and by determining the soluble part in per cents. of the total soluble.

We proceeded the following way.

Twenty-five cc. tannin solution (analytical strength) were shaken out with 25 cc. ethylacetate in a small shaking funnel, the two layers allowed to separate and the aqueous layer run into a second funnel, where the shaking out with another 25 cc. ethylacetate was continued. This process was repeated until the ethylacetate layer appeared quite colorless (2-5 times). Twenty cc. of the remaining aqueous layer were then evaporated, the residue dried until constant weight, and the difference between this weight and the residue of 25 cc. original solution expressed in per cents. of the original solubles.

This gave the solubility in ethylacetate.

The results are given in Table 3 (first column).

It is clearly to be seen that different tannins differ widely in their solubility in ethylacetate. This will specially be of interest for the distinction of different catechol tans, *e.g.*, quebracho and mangrove. The influence of sulphiting quebracho extract is also very distinct, and it can be seen that the more SO_2, the less solubles in ethylacetate. By acidifying the tannin solution with acetic acid before shaking out with ethylacetate, somewhat higher figures are obtained; but they never come up to the figures of original quebracho (see figures in brackets). The fact that wood pulp is not or very little soluble in ethylacetate is also worth mentioning. Applications of this test will be given later, but it may be said here, that much experimental work in this direction is needed, to corroborate the figures given here, to learn the limits for each tannin and to determine the influence of different methods of extract manufacture on the figures of one material. Further on other solvents than ethylacetate have to be tried.

It would be interesting to investigate what percentage of tannins and non-tannins are shaken out with ethylacetate; we have done such an analysis in one case, viz., in the case, of a quebracho extract. By shaking out 100 cc. of a 1 per cent. solution of a

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liquid quebracho extract four times with 100 cc. ethylacetate, evaporating the ethylacetate (at low temperature) and dissolving the residue in 300 cc. H_2O, bringing the aqueous layer as well to a volume of 300 cc., the analysis of these two solutions gave the amount of tans and non-tans which are soluble in ethylacetate. We found:

Soluble in ethylacetate { 90.56 per cent. of the tans
43.9 per cent. of the non-tans
77.7 per cent. of the solubles.

TABLE III.

	Soluble in ethylacetate Per cent.	Precipitated with alcohol Per cent.
Quebracho 1	77.9	2.2
" 2	72.7	2.2
" 3	80.0	0.8
Sulf. Quebracho 1 (3.18 per cent. SO_2[1])	33.6	4.7
" " 2 (4.3 per cent. SO_2)	31.1 [44.1]	2.1
" " 3 (6.47 per cent. SO_2)	23.9 [31.1]	1.1
Mangrove 1	4.9	6.8
" 2	0.0	1.3
Ulmo	26.0	1.6
Mimosa 1	34.2	2.3
" 2	37.9	0.0
Gambier (indragiri)	51.4	4.8
Oakwood	2.0	26.7
Chestnut 1	3.0	21.3
" 2	10.1	17.4
" 3 (decolor.)	9.4	19.1
Myrobalans 1	33.3	9.3
" 2	35.7	8.2
" 3	44.4	8.2
" 4	45.6	5.5
Valonia 1	7.3	38.6
" 2	0.3	26.0
Sumach 1 (extract)	50.7	14.8
" 2 "	56.2	10.5
" 3 "	57.7	9.8
" 4 (Sicilian sumach)	42.0	15.9
Divi-divi	49.7	1.8
Algarobilla	54.4	1.4
Pistacia	3.4	28.9
Gallotannic acid	91.8	0.0
Wood pulp 1	0.0	37.1
" " 2	0.0	52.2
" " 3	3.9	43.3
" " 4	3.9	71.7

[1] Per cent. of solubles.

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Thus the solubility of the quebracho tans is about as high as the solubility of gallotannic acid (see Table III). (But they are not identical as can be seen from the acetic acid lead acetate test, which gives clear solution with quebracho, but copious precipitation with gallotannic acid.)

Another solubility test was carried out by adding alcohol to the aqueous tan solution as follows:

Ten cc. tannin solution (6-8 times analytical strength) were put in a 100 cc. flask and alcohol (95 per cent.) added to the mark; after shaking the flask and allowing it to stand for about one hour, the precipitate was filtered, and 50 cc. of the filtrate evaporated, dried to constant weight and the difference between this weight and half of the solubles in 10 cc. of the original tannin solution expressed in percentage of the original solubles. This gave the alcohol precipitation figure.

The second column in Table III contains the results.

All catechol tans seem to give very low figures. The high figures of wood pulp may also be mentioned.

The remarks made with regard to the ethylacetate figures may also be applied here; and it is to be hoped that the application of other organic solvents (acetone, methylalcohol, etc., and mixtures) will lead to some more valuable figures.

Applications of Solubility Tests.

Only a few of them may be given as examples.

A pure unsulphited quebracho extract must give an ethylacetate figure of 70-80 per cent. and an alcohol figure of less than 3 per cent.

Presence of wood pulp diminishes the first and increases the last figure considerably. Mixtures which we made prove this and show that the ethylacetate figure very nearly agrees with the figure calculated from the figures of the components.

	Ethylacetate figure		Alcohol figure
	found	expected	
In 250 c.c. { 14 g. quebracho + 7 g. wood pulp }	44.4	46.9	21.5
In 250 c.c. { 20 g. quebracho + 2 g. wood pulp }	66.6	65.5	5.5

Thus, if unsulphited quebracho extract contains no pyrogallol

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tans (see formaldehyde test), and gives low ethylacetate and high alcohol figures the presence of wood pulp is to be inferred.

If, on the other hand, the ethylacetate figure is lowered, but the alcohol figure unchanged, and neither pyrogallol tans nor wood pulp found by the respective tests, the adulteration of the quebracho extract will be due to either mangrove or some other catechol tan (f. i. ulmo).

The following experiment, made on a mixture of quebracho and mangrove bears this out.

	Ethylacetate figure		Alcohol figure
	found	expected	
In 250 cc. { 11 g. quebracho + 7 g. mangrove }	38.9	37.4	3.3

The ethylacetate figure is not only qualitative but also gives us an idea of the amount of adulteration in a quebracho extract.

Another application of the solubility tests applies to the detection of myrobalans in mixture with oakwood or chestnut extracts. The ethylacetate figure will appear increased and the alcohol figure diminished.

A chemical detection of adulterations of sumach may also be carried out by this test, as is illustrated in the following table:

	Ethylacetate figure		Alcohol figure
	found	expected	
Sumach	42.0	—	15.9
90 % sumach + 10 % pistacia	36.8	38.1	16.0
75 % sumach + 25 % pistacia	31.8	32.35	18.4
50 % sumach + 50 % pistacia	24.2	22.7	20.0
Pistacia	3.4	—	28.9

This may be useful as a supplement to the microscopical analysis, allowing us to assume the approximate amount of pistacia present. Sumach containing stems (and thus showing a smaller amount of tans by analysis) behaves like ordinary sumach (*e.g.* 45.2 per cent. ethylacetate figure; 10.7 per cent. alcohol figure).

Several other applications of the solubility tests can easily be suggested after studying the table.

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I. Attempts to Get Iodine Values of the Different Tannins.

The action of iodine on tannins has been studied by Boettinger,[1] Jean,[2] Boudet[3] and lately by Hinrichsen and Kedesdy.[4] The last named authors investigated carefully the influence of different conditions on the iodine number of gallotannic and gallic acid, and they have worked out a method which gives reliable and concordant results, showing that one molecule of gallotannic acid combines with 16 atoms of iodine, while one molecule of gallic acid combines with 8 atoms of iodine.

We have adopted the method of Hinrichsen and Kedesdy, working in the following way:

Twenty-five cc. tannin solution (containing about 0.1 tannin) + 20 cc. iodine solution (about one-third normal) + about 2 grams $NaHCO_3$ were allowed to stand over night and then titrated back with one-third N-thiosulphate.

The same test was carried out with 30 cc. of the non-tan solution, which corresponds to 25 cc. of the above tannin solution. The figures thus obtained and the weights of the residues of solubles and non-tans allowed us to calculate how many grams iodine are taken up by (*a*) 1 gram solubles, (*b*) 1 gram non-tans (*c*) 1 gram tannin.

It was hoped that these figures would come out in good concordance when different samples of one tannin material or extract were used, and that different tanning materials would differ widely in their iodine numbers. This being the case, the iodine number would be a very valuable factor in the examination of tannins. Unfortunately our expectations were not realized by the experiment as can be seen from table IV. We communicate these results in order to save the time of anybody who intends to work in this direction. Some few observations may also be mentioned which we made in the course of these experiments. We found that in the case of quebracho, mangrove, ulmo, gambier and pistacia lentiscus, a precipitate was formed with iodine and sodium bicarbonate, while the solutions of oakwood, chestnut,

[1] Chem. Zeitung, 1896, p. 984; 1897, p. 57 and 460.

[2] Ann. chim. anal. appl., 5, p. 134.

[3] Bull. Soc. Chim., 3, 35,769, 1906.

[4] Mitteilungen aus dem königlichen materialprüfungsamt, Gross-Lichterfelde, Berlin, 1907. See also Grasser, Coll., 1910, p. 408, and 1911, p. 46.

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mimosa, myrobalans, sumach and wood pulp remained clear. The non-tans remained clear in all cases. This shows about the same classification as the Eitner-Philip test. The iodized solutions of all tannins no longer give tannin reactions; even the formaldehyde pecipitation is not given by the iodized catechol tans. This proves that the iodine reacts with the hydroxyl groups, which is in concordance with Boettinger's statement that acetylated tannins do not take up any iodine.

TABLE IV.

	Iodine numbers of			
	Solubles	Tans	Non-tans	Hydrolyzed solubles
Quebracho	4.45	3.82	8.38	4.51
"	4.28	3.89	7.67	4.07
Mangrove	3.21	3.41	2.64	3.02
Ulmo	3.9	3.71	5.9	4.85
"	2.15	3.85	1.3	——
Mimosa	4.23	4.56	3.4	3.24
Gambier	2.93	3.07	2.73	2.78
Oakwood	3.32	3.9	2.14	2.4
Chestnut	3.95	3.5	5.8	2.8
"	4.36	4.55	4.35	——
Myrobalans	3.7	4.44	2.41	2.14
Sumach	4.1	5.58	1.58	——
"	4.44	5.37	2.77	——
"	4.66	6.3	1.6	——
Wood pulp	0.88	——	——	0.89
" "	0.96	——	——	0.89

We have also determined the iodine numbers of tannins, after boiling the solutions with alkali and acidifying the hydrolyzed solutions with acetic acid. Fifty cc. of the tannin solution (analytical strength) were taken and 5 cc. sodium hydrate (40 per cent.) added, and the mixture boiled with the reflux condenser for two hours; then the solution was made up to 100 cc., 50 cc. out of it was taken, slightly acidified with acetic acid and treated with 25 cc. iodine solution and 2 grams sodium bicarbonate as before. We expected to see some valuable relation between this iodine number and the iodine number of the original solutions, assuming that the different splitting up products of the various tannins should behave differently against iodine. The last column of Table IV shows that even this expectation was not realized by this experiment.

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	Ethylacetate fig. (see p. 489)	Alcohol figure (see p. 490)	5 cc. tannin solution of analytical strength: + 5 cc. lead acetate (10 per cent.) filtrate + Na OH	+ 5 cc. basic lead acetate (10 per cent.) filtrate + Na OH	+ 10 cc. acetic acid (10 per cent.) + 5 cc. lead acetate (10 per cent.):	Filtrate + ferric alum	Filtrate + ferric alum + sodium acetate	+ 10 c.c. tartar emetic (4 per ct.)	50 cc. tannin solution (anal. stren'th) + 5 cc. strong HCl + 10 cc. HCHO (40 %): during 15 min. boiling	Filtrate + ferric alum + sodium acetate	5 cc. tannin solution (6–8 × anal. strength) + 10 cc. ammonium acetate (40 %)	2–3 cc. tannin solut. (0.1 × anal. strength) + 3–5 drops $CuSO_4$ (1 %) + 3 cc. NH_3 (5 %)	Eitner-Philip test see p. 485
Quebracho 1	77.9	2.2	yellowish	colorless	no pp	green	violet	clear	pp	no coloration	clear	no pp	no pp
Quebracho 2	80.0	0.8	"	"	"	"	"	"	"	"	"	"	"
Quebracho 3	72.7	2.2	"	"	"	"	"	slightly turbid	"	"	"	"	"
Quebr. sulf. 1	33.6	4.7	"	"	slight pp ($Pb\ SO_4$)	"	"	clear	"	"	"	"	"
Quebr. sulf. 2	31.3	2.1	"	"	"	"	"	"	"	"	clear (after 24 h turbid)	"	"
Quebr. sulf. 3	23.9	1.1	"	"	"	"	"	"	"	"	"	"	"
Mangrove 1	0.0	1.3	colorless	"	no pp	"	"	"	"	"	clear	"	"
Mangrove 2	4.9	6.8	"	"	"	"	"	"	"	"	"	"	"
Ulmo	26.0	1.6	yellowish	"	"	"	"	slightly turbid	"	"	"	"	"
Gambier	51.4	4.8	"	"	"	"	green	turbid	"	"	"	"	"
Mimosa 1	34.2	2.3	colorless	"	"	deep bluish violet	deep bluish violet	pp	"	"	"	pp (over night)	pp
Mimosa 2	37.9	0.0	"	"	"	"	"	pp (after standing over night)	"	"	"	"	"
Pistacia	3.4	28.9	yellow	"	pp	green and violet	dirty green and violet	pp.	"	deep bluish violet	"	no pp	"
Chestnut 1	3.0	21.3	colorless	"	"	faint violet	violet	"	clear	"	pp	pp	"
Chestnut 2	10.1	17.4	"	"	"	"	"	"	"	"	"	"	"
Chestnut 3	9.4	19.1	"	"	"	"	"	"	"	"	"	"	"
Oakwood	2.0	26.7	"	"	"	no coloration	no coloration	"	"	"	"	"	"
Myrobalans 1	33.3	9.3	"	"	turbid	deep bluish violet	deep bluish violet	"	turbid	"	"	pp (over night)	"
Myrobalans 2	44.4	8.2	"	"	pp	"	"	"	pp	"	pp (after 2h standing)	no pp	"

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	Ethylacetate fig. (see p. 489)	Alcohol figure (see p. 490)	5 c c. tannin solution of analytical strength					50 cc. tannin solution (anal. strength) + 5 cc. strong HCl + 10 cc. HCHO (40 %)		5 cc. tannin solution (6–8× anal. strength) + 10 cc. ammonium acetate (40 %)	2–3 cc. tannin solut. (0.1× anal. strength) + 2–3 drops $CuSO_4$ (1 %) + 3 cc. NH_3 (S %)	Bitner-Phillip test see p. 485
			+ 5 cc. lead acetate (10 per cent.) filtrate + Na OH	+ 5 cc. basic lead acetate (10 per cent.) filtrate + Na OH	+ 10 cc. acetic acid (10 per cent.) + 5 cc. lead acetate (10 per cent.)		+ 10 cc. tartar emetic 4 per cent.	during 15 min. boiling	Filtrate + ferric alum + sodium acetate			
						Filtrate + ferric alum	Filtrate + ferric alum + sodium acetate					
Myrobalans 3	45.6	5.5	colorless	colorless	pp	deep bluish violet	deep bluish violet	pp	pp	deep bluish violet	pp (after 2h standing)	pp
Myrobalans 4	35.7	8.2	"	"	"	"	"	"	"	"	pp (after standing over night	"
Sumach 1	57.7	9.8	yellow	"	"	violet	violet	"	"	"		pp
Sumach 2	59.7	14.8	"	"	"	"	"	"	"	"		"
Sumach 3	56.2	10.5	"	"	"	"	"	"	"	"	turbid "	"
Sumach 4	42.0	15.9	"	"	"	"	"	"	"	"	"	"
Valonia 1	7.3	38.6	colorless	"	"	no coloration	no coloration	"	slig'tly turbid	"	pp	"
Valonia 2	0.3	26.0	"	"	"	"	"	"	"	"	"	"
Divi-divi	49.7	1.8	"	"	"	violet	violet	turbid	"	"	"	turbid
Algarobilla	54.4	1.4	"	"	"	"	"	"	"	"	"	"
Gallotannic acid	91.8	0.0	"	"	"	deep bluish violet	deep bluish violet	clear	"	no coloration	see p. 485	no pp
Wood pulp 1	0.0	37.1	deep yell'w	yellow	no pp	no coloration	no coloration	"	clear	"	"	pp
Wood pulp 2	0.0	52.2	"	"	"	"	"	"	"	"	"	no pp
Wood pulp 3	3.9	43.3	"	"	"	"	"	"	"	"	"	pp over night
Wood pulp 4	3.9	71.7	"	"	"	"	"	"	"	"	"	no pp

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We have therefore not continued the study of iodine numbers, though it is possible that the action of iodine on tannins may still be useful in some other way for the differentiation of tannins. If we, for example, take quebracho, dividing the solubles into those soluble in ethylacetate and those which are insoluble, and then determining the iodine numbers in both parts, we might get some useful information not only as regards the difference in the behavior of these two parts to iodine, but also as to the analogy of the ethylacetate fractions of different materials. In choosing a number of organic solvents, and determining the iodine values of the tans and non-tans of different materials soluble in these solvents, we might find corresponding figures which allow the conclusion that one component in the complex mixture of a tanning material is identical with one component in another tanning material. This of course means working in a somewhat different direction than was the original object of this paper.

Turning back to the promising tests mentioned above, we think it convenient to reproduce the behavior of the different tannins in table form (Table V). We trust that this table will not only help us considerably to distinguish a pure extract, but will also enable us in many cases to decide as to the nature of a mixture.

Before concluding, we wish to repeat once more that the results given above are only to be taken as a small step in the work of qualitative examination of tannins. Though the figures which we communicate are obtained by careful work and are reliable for the tannin extracts which we had in hand, we fully recognize the necessity that a far greater number of experimental figures of different samples must be obtained—by collaboration of many workers—in order to get reliable mean values, and limit values for each tannin and in order to learn the effect of different treatments of extracts even if no adulteration is added. We hope that this paper will give stimulation for such work.

SOME LABORATORY NOTES ON DIVI-DIVI.

By C. R. Oberfell.

A known sample of Mexican divi-divi (cascalote) gave the following results on analysis by the methods of this Association.

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	Per cent.
Moisture	8.50
Absolutely dry basis	
Total extractive	81.94
Total soluble	80.24
Insoluble	1.70
Non-tannin	29.42
Tannin	50.82
Glucosides as glucose	14.13

The color on a sheep skiver from 1.0 per cent. solution closely resembled that of Sicilian sumac, perhaps with a slight yellow cast. This solution when two weeks old and containing 0.25 per cent. acid as acetic developed a reddish cast and gave a skiver test several shades darker than that obtained from the fresh solution, and closely resembled a test from "Red" oak bark.

ABSTRACTS.

Quinone Tannage. Prof. L. Meunier in Tanners' Year Book, 1911, p. 75.—Hide absorbs 1.5 to 2 per cent. of quinone, the product being a tough, thin-grained leather, unaffected by boiling. Such leather is, however, very "flat," and except for a few special purposes, the process is therefore not practical. Preliminary tannage with quinone, followed by any good vegetable tanning agent gives very good results, particularly in sole leather. From three to four-tenths of one per cent. of quinone is used in the preliminary tannage, and it is found that the penetration of the quebracho or other tanning material is much more rapid than in the case of untreated hide.

Non-tannins and Pseudo Tannins. Dr. R. Lepetit, in Tanners' Year Book, 1911, p. 82.—Dr. Lepetit calls the mineral materials of sulphited extracts "honest non-tannins," and claims that in mangrove extract analysis shows as tannins substances that are really not tannins. These he calls pseudo-tannins, and asserts that mangrove extracts are "poor tanning material," and that it is "problematical" whether "the use of mangrove extracts could present any utility." He also classes as pseudo-tannins the matters reported by ordinary analysis in sulphite-cellulose extract as tannin.

Tanning in Afghanistan. By E. T. Thornton, Tanners' Year Book, 1911, p. 102.—This is an interesting account of the author's experiences in introducing into Afghanistan, western methods of tanning.

Notes on Valonia. Tanners' Year Book, 1911, p. 123.—The quality of valonia is largely dependent on the locality from which it comes. Of that received in Smyrna the crop from four districts is rated as "best,"

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amounting to 14,000 tons yearly, "good" growths are received from 14 districts, amounting to more than 25,000 tons, while nine growths are rated as "fair to poor," the total of which is about 16,000 tons. The quality of the yield from any district depends somewhat on the rainfall. The more brittle growths are richer in tannin, having less woody fiber. Closed cups have more tannin than open ones. Some of the growths do not keep so well as others. The best qualities go almost entirely to Austria and Russia. The difference in price between average grades and the best is often as much as $10 per ton.

Smoke Tannage in China. Tanners' Year Book, 1911, p. 127.—Only heavy hides are used, as the smoke shrivels them. The preparation involves liming and unhairing by methods not unlike our own. The fleshings from sole are boiled and make low grade glue. A second paring is given the hides intended for uppers, and these parings make a high grade glue. The hides are smoked in mud-walled rooms. First coarse grass is used, then twigs and branches, and lastly large pieces of wood. The whole process takes only a week, the hides being frequently handled. Much of this leather is exported to Siberia. The price of the sole leather is equivalent to about 73 cents per pound. It is, of course, very light in weight.

The Analysis of Chrome Leather. W. FAHRION. *Collegium*, 1911, 205. —To determine whether chrome leather is sufficiently de-acidified, 2 grams finely rasped leather are warmed with 10 cc. of 8 per cent. alcoholic NaOH, the alcohol evaporated, residue acidulated with HCl and evaporated to dryness. On re-solution, the Cr is precipitated with NH_3 and SO_3 determined in the filtrate with $BaCl_2$ as usual. In this way, 5.32 per cent. Cr_2O_3, 3.59 SO_3 were found, or a ratio of $Cr_2O_3 : SO_3 = 1.48 : 1$. According to Stiasny, the salt $Cr(OH)SO_4$ (ratio 0.95 : 1) has marked tanning power, hence the above leather was too much de-acidified. The author, however, found earlier (abstract, this JOURNAL, **5**, 73) that chromed hide powder, after de-acidifying with borax and showing thorough tannage by the hot water test, analyzed $Cr_2O_3 : SO_3 = 1.56 : 1$. The above leather may then be rated as sufficiently de-acidified. W. J. K.

The Analysis of Chrome Leather. GEORG GRASSER. *Collegium*, 1911, 247-8.—Referring to the above method, the writer makes the objection that it is not certain that all the Cr in the leather is present as basic sulphate, $Cr(OH)SO_4$; also HCl, is used instead of H_2SO_4 in many tanning liquors. He prefers his own method of direct titration of the free acid (abstract, this JOURNAL, **5**, 528) which takes no account of the Cr ratio. W. J. K.

The Analysis of Chrome Leather. II. W. FAHRION. *Collegium*, 1911, 310-11.—Replying to the above, the author admits that the ratio $Cr_2O_3 : SO_3$ may vary in equally good leathers, but asserts it should be possible in time to fix upper and lower limits. As to the influence of HCl when used in the manufacture or present in the reagents, this may be corrected for by computation from analysis. Grasser does not publish any check

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analyses confirming the reliability of his method. Especially should a blank experiment with acid upon unchromed hide be made, since the hide itself may yield acids. The author has earlier shown (*Chem.-Ztg.*, 1902, 676) that on treatment of hide with alkali, the saponification number rose from 44 after 10 minutes to 204.9 after 12 hour's heating. Until it is shown that hide yields only neutral substances, Grasser's method cannot be depended upon. W. J. K.

Brittle Grain in Sole Leather. W. EITNER. *Gerber*, 1911, 37, 157-8, 171-2, 185-7.—This fault in the old fashioned tannage, occurred oftenest with knoppern and valonia tanned sole leathers, either from over-drying (often at 75° C.) or from tanning with valonia in the lay-aways without a sufficient fore-tannage in weak pine liquors. The first error could be repaired by exposing the leather to moist air; the second was irreparable.

In modern sole leather manufacture, the employment of materials (such as valonia, myrobalans) containing "hard" tans, in the handlers, may cause brittle grain. A portion of the tanstuff, ellagotannic acid, is converted into ellagic acid and this is deposited as a powder within the grain fiber, rendering it hard and brittle. If the fore-tannage be carried out with milder materials, the grain may then resist the intrusion of ellagic acid and valonia be used for the effectual tanning through in the lay-aways. Easily soluble cold extracted tans are best for the handler liquors and the residual material may be hot extracted for the finish tannage. The sour liquors prepared by extracting spent valonea from the lay-aways may be used for the handlers without injury to the grain if they be allowed to first ferment a few days; the formation of ellagic acid will then be over.

Another cause of brittle grain observed by the writer is the action of strong mineral acid upon the hide before the tannage has sufficiently advanced. The effect of concentrated organic acids, for example, butyric acid, upon hide substance is similar to that of heat, namely to convert it into glue. Mineral acids act likewise, although in lesser degree, affecting the fine fiber of the grain only. The author describes in illustration a defective leather sent from a Russian tannery which had used sulphuric acid for swelling. The grain was glassy and brittle at all stages of the tannage, showing that the evil originated at the start and was not due to the tanning. If sulphuric acid is to be used for swelling, the hide should first be lightly tanned in sweet liquor to prevent two vigorous an attack of the acid. This precaution is especially needful when butyric acid is used. The glassy, brittle grain from these causes cannot be restored to its normal state, but the hardness may be reduced by rubbing with and drawing through a 5 per cent. alum solution. After lying 12 hours, a 5 per cent. formaldehyde solution to which ½ per cent. calcined soda has been added is applied as above and after standing several hours, an emulsifiable oil, like carbidol or moellon, is rubbed in. The above treatment directly, follows the tannage. If the leather is already dried, it must first be softened with a 4 per cent. soda solution.

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In another example, a sole leather was first tanned in handler liquors to which oxalic acid had been added. One lot was then finished in pits and gave a leather with dark, brittle, horny grain, showing little tannage of the surface. A second lot was finished in the drum and was perfect, showing that the mechanical treatment promoted the tanning through of the grain.

In conclusion, in the normal process, the swelling proceeds in natural sour liquors, beginning with the weakest, the upper vats being strengthened or freshly charged with liquor which is highest in acid. The acid is more rapidly consumed than the tannin, hence the lower vats are weak in acid and permit a light fore-tannage in advance of the swelling and the grain will not be later attacked by acids. The new fashion of adding organic acids to the first vats or giving a preliminary swelling with sulphuric acid is responsible for the brittle grain. To avoid this, a light fore-tannage in sweet liquors of 12-15° should precede as first practised in America. Formic acid is as well suited for plumping as lactic or butyric acids, and there is less danger of grain fracture. W. J. K.

Contributions to Qualitative Tests of Tannins. J. SCHNEIDER AND A. SEIWERTH. *Collegium,* 1911, 282-4.—The first method discussed is the dyeing effect of various tannin solutions upon cotton previously mordanted with metallic salts. The alkali earths, Mg, Sb, Mo, W, give no color; Zn, Cd, Hg, Sn, Pb are weak. Towards salts of Fe, Al, Cu, Ti, Zr, Ce, Th, V, Bi, Cr, U, Ni and Co, tannin extracts act as polygenetic dyestuffs; the colors are weakened by previous reduction of the tannin solution with hydrosulphite and intensified by a corresponding oxidation in a stream of air. The various colors are tabulated and grouped, ranging from greenish yellow (sumac, myrobalans) to brown yellow (catechu) with Al, yellowish brown (chestnut wood) to dark brown (catechu) with Ti, colorless (oakwood) to red brown (mangrove) with Zr, yellow (valonia) to chocolate brown (mimosa) with Bi. Mangrove differs from quebracho only with Al, Zn, Pb and V, being somewhat darker. Myrobalans differs strongly from quebracho and mangrove, giving lighter colors with Al, Cu, Zr, Sn, Ce, Pb, Th, Bi, Cr, U, Ni and Co and a different black with V and Fe. Chestnut and oakwoods show little distinction.

The second method employs spectral absorption, following Formanek's "Spectral analyse." Aqueous solutions of most tanning materials show no characteristic spectra; alcoholic solutions give the best results and the oriented lines for various tannins are tabulated. The positions of most agree closely with those given by Formanek for chlorophyll. Amyl alcohol and acetone solutions are also tabulated. The results with freshly prepared solutions are quite different from those yielded by commercial extracts. Old sumac and myrobalan extracts gave no lines whatever. The method requires further testing and will hardly be so reliable as dyeing tests. W. J. K.

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PATENTS.

Leather-working Machine. U. S Patent No. 1,002,879. JOSEPH STANISZEWSKI, Wilmington, Del.

Process of Bating Hides. U. S. Patent No. 1,003,124. OTTO RÖHM, Darmstadt, Germany.

Enzymes of pancreatic juice are employed in a fermenting liquor, containing salts of ammonia or an alkali or both. Trypsin of vegetable origin is also used.

Process for Treating Hides. U. S. Patent No. 1,003,205. DANIEL REDDAN, Fitzroy, Victoria, Australia.

The hides are dehaired in the ordinary manner, and then treated with alum, arsenic, soft soap and caustic soda. Then a "rubber dough" mixture is worked in, containing rubber, (or a mixture of rubber and reclaimed rubber), pulverized asbestos, zinc oxide, sulfur, paraffine, beeswax, tallow, lamp-black and litharge, and finally "curing" by means of heat.

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Journal of the

American Leather Chemists Association

Vol. VI NOVEMBER, 1911 No. 11

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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NEW OFFICERS OF THE ASSOCIATION.

Our President, Mr. Joseph H. Russell, having resigned his office, the Council, in accordance with By-law 5, have elected Mr. F. P. Veitch to fill the vacancy. To fill the office of Vice-President thus rendered vacant, Mr. R. W. Griffith was chosen. To fill the unexpired term of Mr. Griffith as ordinary member of Council, Mr. C. R. Oberfell was elected.

H. C. REED, Secretary.

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EIGHTH ANNUAL MEETING.

The eighth annual meeting of the American Leather Chemists Association will be held at Washington, D. C., December 7, 8 and 9, 1911. The committee having in charge the arrangements for the meeting has selected the Hotel Raleigh, Pennsylvania Ave. and 12th St. as the place of meeting. A suitable room has been reserved for the meetings, and members who desire to retain rooms at the hotel are requested to apply directly to the management. The following is the schedule of prices:— Single rooms, $2 per day and up; with bath, $3 per day and up; double rooms, $3 per day and up; with bath, 4 per day and up.

The program of the meeting, so far as arranged, is as follows:—

THURSDAY, DECEMBER 7TH.

Morning Session:—

Opening remarks by the President.

Report of the Secretary-Treasurer.

Committee reports.

Afternoon Session:—

Address by Mr. E. C. Alsop, "Purification of Liquid Tannery Waste by Forced Oxidation."

Address by Mr. A. W. Hoppenstedt, "Seal Oil."

Address by Mr. Geo. A. Kerr, "Notes on the Acids and Acid Forming Value of Chestnut Wood and Chestnut Oak Bark Liquors and Extracts.

FRIDAY, DECEMBER, 8TH.

Morning Session:—

Committee reports.

Address by Mr. C. R. Oberfell, "The Composition of Leather from Different Parts of the Hide and the Importance of a Proper Sample for Analysis."

Afternoon Session:—

Address by Mr. A. H. Lockwood, "The Development of the Leather Industry in its Relation to the World's Hide Supply."

Address by Mr. A. W. Hoppenstedt, "The Tannins."

Address by Mr. William M. Norris, "Chrome Methods."

SATURDAY, DECEMBER 9TH.

Morning Session:—

Address by Mr. R. W. Griffith, subject to be announced.

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Business matters.

There will also be a paper by John H. Yocum, subject to be announced, and a paper by Henry W. Healy, "Are Tanners Teaching their Superintendents how to Think?"

THE FILTRATION OF TANNIN ANALYSIS SOLUTIONS UNDER REDUCED PRESSURE.

By Charles R. Oberfell.

In 1907[1] Reed presented a method for the filtration of tannin analysis solutions under diminished pressure, and since that time each year up to the present, there has been a Committee of the American Leather Chemists Association investigating this method. Previous to this the American Leather Chemists Association experimented with the "Berkefeld Candle Filter" of the International Association of Leather Trades Chemists, but discarded it on account of a number of objections. Recently Procter[2] compared the Berkefeld Candle Filter with the "Asbestos-Kaolin" method of Reed, and obtained results which are comparable.

The writer served on the American Leather Chemists Association Committee which investigated this subject for three years and was continually impressed with the fact that the forms of apparatus proposed together with the difficulty of obtaining a uniform filtering matt, from time to time, militated against the method.

The recent introduction of "Alundum" as a filtering medium suggested a suitable substitute for the uncertain asbestos matt, and the form in which this material is made, *i.e.*, that of a dish giving a large filtering surface, promised adaptability providing it removed the insoluble material perfectly.

This investigation therefore was undertaken in order to determine whether or not the alundum would properly filter tannin solutions.

Alundum[3] is put out in three mixtures representing as many

[1] This Journal, Vol. II, 420.

[2] *Collegium*, 1910. Report of the Chairman of the International Committee on Tannin Analysis.

[3] Alundum is made by fusing the mineral bauxite in the electric furnace and is practically pure fused alumina. It is manufactured by the Norton Company, Worcester, Mass., to whom is due recognition for kindly supplying the various forms used in this work.

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degrees of fineness, and it is designated in the following manner proceeding from the coarse to the finest mixture—RA 98, RA

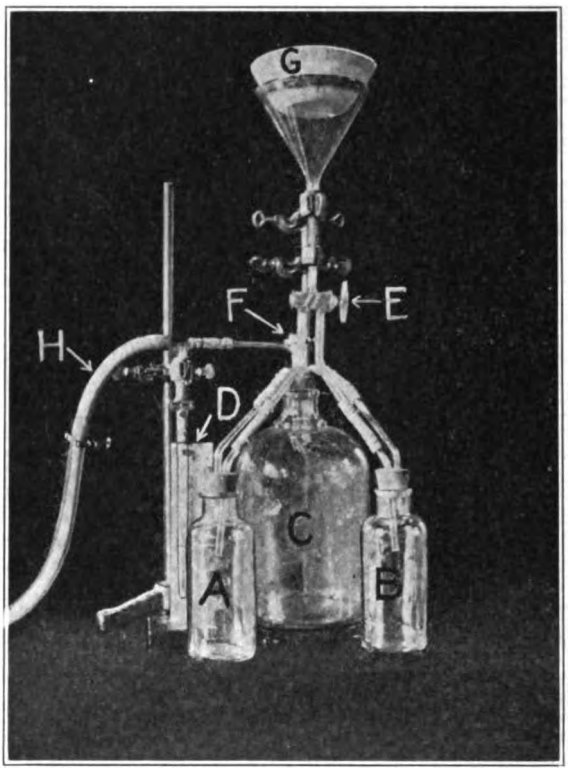

Fig. 1.

184 and RA 84. The dish is 45 mm. deep with a bottom diameter of 65 mm. and top diameter of 140 mm.

Fig. 1 is the apparatus used in these experiments.

DESCRIPTION OF APPARATUS AND METHOD OF MANIPULATION.

G is the alundum dish and contact between the dish and funnel is obtained by means of a soft rubber ring.[1] E is a two-way cock connecting the collection jars A and B, which in turn are connected to the vacuum chamber C. D is a mercury vacuum gauge connected to the pump through tube H. F is a valve to break the vacuum.

[1] This is made by cementing together the ends of a pure gum tube.

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TABLE I.

	Dish "RA, 98" + kaolin											Official filtration			
					Vacuum										
Extract	Grams of kaolin	Time of digestion, minutes	Discarded solution, cc.	Discarded solution, time, min.	Start mm.	Finish mm.	Collection 100 cc., time, sec.	Weight ϕ	Per cent.	Appearance of filtration	Total time Min. Sec.	Weight	Per cent.	Appearance of filtrate	Total time min.
Chestnut wood	5	5	400	2	58	58*	45	0.5718	38.12	Clear	7, 45	0.5715	38.10	Clear	82
Chestnut wood	3	5	400	2	57	27	45	0.5724	38.16	Clear	7, 45	0.5715	38.10	Clear	82
Ordinary quebracho	3	5	300	3	55	50	180	0.5017	41.12	Slight opalescence	11, 0	0.5003	41.01	Slight opalescence	130
Ordinary quebracho	3	5	200	1	50	50	90	0.4670	42.45	Slight opalescence	2, 30	0.4695	42.68	Opal-escent	100
Treated quebracho	3	5	300	2	52	40	20	0.5264	42.46	Clear	7, 20	0.5244	42.29	Clear	89
Oak bark	3	5	300	3	50	30	50	0.6366	42.44	Clear	8, 50	0.6360	42.40	Clear	100

TABLE II.

	Dish "RA, 184"											Official filtration			
Chestnut wood	—	—	200	20 sec.	25	25	10	0.5886	39.24	Clear	0, 30	0.5875	39.17	Clear	88
Ordinary quebracho	—	—	400	2 min.	50	50	40	0.4663	42.39	Slight opal.	2, 40	0.4695	42.68	Opal.	100

TABLE III.

	Dish "RA, 84"											Official filtration			
Chestnut wood	—	—	100	1	50	45	1 min.	0.5893	39.29	Clear	2, 0	0.5875	39.17	Clear	88
Ordinary quebracho	—	—	100	5	40	50	46 min.	0.4540	41.27	Clear	51, 0	0.4585	41.64	Slight opal.	130

* Filtration too vigorous.

ϕ Average of duplicates.

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To conduct the filtration cock E is closed and the vacuum run up to any desired point. The solution is poured into the dish, cock E is opened into A where collection is made until the filtrate comes clear. E is then turned into B where the solution for evaporation and drying is collected.

EXPERIMENT WITH DISH RA 98.

This dish, which is of the coarse mixture, failed to remove the insolubles from such materials as ordinary quebracho, and the experiment was conducted by forming a film of acid washed kaolin on the filtering surface. This necessitated the digestion of the solution with the kaolin to satisfy any tendency to absorb tannin. Results are given in Table I.

EXPERIMENT WITH DISH RA 184.

This dish, which is the medium mixture, removed more insoluble material than RA 98 with kaolin, and had about the same speed of filtration. Results in Table II.

EXPERIMENT WITH DISH RA 84.

This dish, which is the finest mixture, removes all of the insoluble material, but the rate of filtration is materially reduced over the other two. Results in Table III.

A study of the results indicates that within the error accompanying evaporation and drying and the weighing of uncovered desiccated residues the alundum is a favorable medium for the filtration of tannin solutions, that it does not absorb tannin and is capable of very rapid manipulation.

The dish may be readily prepared for subsequent filtrations by treatment with hot water, or where this fails with hot alcohol, and drying. Such a treatment will at least remove all soluble tannin with the greater portion of the insolubles, but if it is desired to return it to its original state of cleanliness this can be accomplished by ignition[1] when all residue on account of its organic nature is removed.

Harrisonburg, Virginia.

October, 1911.

[1] Least likelihood of fracture is obtained by using a radial burner at least as large as the dish together with shelter from air currents.

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INTERNATIONAL LEATHER TRADES CONGRESS AT TURIN.[1]

The first International Leather Trades Congress met at Turin on September 17, 18 and 19, 1911. About 300 delegates were in attendance, the majority of whom were Italian and French. Other countries represented were Austria, Hungary, Germany, Spain, Switzerland, Belgium and England. The meetings were held in the Hall of the Chamber of Commerce. The first day was devoted to speech-making, inspecting the leather exhibits at the Turin Exposition, and to social gatherings.

The first paper presented on the second day was by Prof. L. Meunier on the cure and preservation of hides and skins in the white condition. He called attention to the faults of the present methods, as giving interest to studies on a new method of the nature of pickling, these processes presenting fewest inconveniences and insuring the fullest degree of preservation. An important point in regard to the pickling process is the fact that it constitutes a valuable preliminary tannage, introducing into the hide an almost negligible weight of material. It does not change the nature of the grain, but keeps it soft and fine, and this characteristic of the grain, once acquired, persists throughout the tanning process and finally is a quality of the finished leather. Work of Prof. Meunier already published[2] has shown that compounds of chlorine, bromine and iodine can, under certain conditions, exert on the hide a pickling action, or preliminary tannage. The action on gelatine was first studied, and it was shown that this substance is easily rendered completely insoluble. A secondary effect also takes place, hydrolytic in character, due principally to the formation of hydrochloric, hydrobromic and hydriodic acids and to their action on the gelatine. This secondary action is disorganizing and should be avoided as much as possible. It may be done in two ways, by cold which retards, or by common salt which counteracts the hydrolytic action. This use of salt is familiar in all the methods of pickling heretofore in use.

Bromine gives the best results from the point of view of insolubility of the gelatine, chlorine next and iodine least. The

[1] This account is taken from the reports in *Leather*, *Leather Trades Review*, *Le Cuir* and *La Halle aux Cuirs*.

[2] See abstract, page 528, this number.

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quantities necessary are at most very small, in the case of bromine about 1 per cent. But in spite of the better results obtained with bromine, the difference in price makes the chlorine process more practicable. Prof. Meunier described a number of experiments. The process which gave the best results was as follows: For 100 kilos of white hide, 300 liters of water and 3 kilos of chloride of lime. To this solution were added 3 kilos of common salt. (200 lbs. white hide, 75 gallons of water, 6 lbs. chloride of lime, 6 lbs. salt.) The skins are soaked in this solution for two hours, then put in storage. Hides treated in this manner, even during the greatest heat of the past summer, remained entirely uninjured for three weeks. They were in condition to take any kind of tannage with great facility, and made leather with the finest grain.

The second paper, on the "Warble in Hides," was presented by M. Gaston Tainturier, Secretary of the French *Chambre Syndicale* for leather, hides and skins. M. Tainturier is also President of the French association for the destruction of the warble. M. Vaney, another French authority on the warble, followed. The discussion of this subject included remarks by many delegates. M. Emile Kamp said that the percentage of warbled hides in Denmark had fallen from 10 per cent. to 1 per cent. in ten years in consequence of persistent squeezing out of the grub from the backs of cattle.

The next paper, on the "Salting of Hides" and the "Denaturing of Salt," was presented by M. Camile Romana and Dr. Baldracco of the Royal School of Tanning in Turin.

"Flaying with the Hammer" was the next subject treated, in a paper by M. Camille Féta. This method of flaying is being introduced into France with very good results. It is also used in the Low Countries and Germany.

The next subject treated was the disposal of tannery wastes. M. Gabriel Jossier, President of the *Chambre Syndicale* for leather, hides and skins, spoke first. He recommended that each country represented conduct experiments on the treatment of each kind of tannery effluent, and that the results of these experiments be tabulated and presented to a future congress. Dr. H. Becker, President of the German section of the I. A. L. T. C. followed, with a report of experiments on methods for the

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purification of tannery effluents. He described each of the methods in present use, I, the method of decantation from settling basins, which often has the disadvantage, especially in certain forms of basins, of producing deposits on the surface due to fermentation. II. Purification by filters of various kinds. Good results are obtained by filtration through spent tan-bark, but this old method has the disadvantage of carrying some tannin into the streams, which in the case of waters containing iron blackens them. III. The biological method. Prof. Becker said that this method often gave more harmful effluents than the tannery wastes themselves. While the tannery wastes do little harm to large rivers, they cause dangerous pollution to small streams, frequently making chemical treatment necessary. Dr. Becker passed in review the different wastes of the tannery, mentioning the different chemical methods of treatment, and expressed the opinion that the best method involves treating each of the separate wastes by itself by appropriate methods. M. Andreis recommended that each country establish a commission on the subject of tannery wastes.

The next topic, sterilization of hides containing anthrax spores, was introduced by Mr. Seymour-Jones in a paper defining the problem and describing his mercuric-chloride-formic-acid method. (See this JOURNAL, Vol. VI, p. 85.) Professor Kohnstein recommended the hydrochloric acid and salt method, (see this JOURNAL, Vol. VI, p. 416), and said that it is being used with great success in Austria. Dr. Becker said that he had used mustard oil successfully. M. Belfante described a method of testing hides for the presence of the anthrax spore. A piece of the hide in question is digested at 80°-90° C. in physiological serum, and the liquid after filtration is poured gently down the wall of a test-tube containing a few cc. of anti-anthrax serum in such a manner that the two liquids do not mix. The formation of a white ring at the junction of the two liquids indicates that the hide came from an animal which died of anthrax. If the hide was not infected the white ring does not appear.

The first topic at the session of September 19th was the unification of methods of analysis. The first speaker was M. Edouard Roy, President of the Tanning and Dyewood Extract Manufacturers' Syndicate of France, who read his paper on unifica-

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tion of methods, prepared in conjunction with M. De la Bruère, President of the French Section of the I. A. L. T. C. His opinion that methods of analysis should be adopted that would show the amount of actual leather-forming constituents in extracts was warmly seconded by Dr. Lepetit, who referred to the presence of sulphite-cellulose extract in many extracts, which the ordinary methods report as tannin, while according to his view it should not be so reported.

Dr. Baldracco read his treatise on the unification of methods of examination of oils and fats used in the leather trades.

At the concluding session the Congress adopted six resolutions. I. Tannery Effluents. The matter is placed in charge of an international commission to report to the next Congress. II, Warble-fly. Each country is urged to prosecute the war on this pest. III, Unification of Methods of Analysis. The Congress recognizes that rigorously exact methods of tannin determination are not at present possible. The details of the I. A. L. T. C., method should be so carefully worked out as to insure concordant results by different analysts. IV, Anthrax. The thanks of the Congress were extended to the authors of the several methods of sterilization, and it was recommended that these methods and others which may be presented be carefully studied. V. Publication of the Proceedings of the Congress. VI. Providing for the appointment of a Provisional Committee to arrange for the next Congress.

THE CHEMICAL CHARACTERISTICS OF LEATHER IN RELATION TO THE AMOUNT OF MINERAL AND ORGANIC MATTER IT CONTAINS.[1]

Presented to the International Congress at Turin by Professor Doctor Baldracco, Director of the Royal Italian Tanning School at Turin.

One of the most important questions which concern the leather industry is that of establishing in a definite manner the chemical characteristics of the ordinary leather of commerce. This question has become more acute of late years because of

[1] From *Leather*, Oct. 5, 1911.

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the development of extract tanning, for one finds in commerce, leather whose weight is due partly to the quantities of tanning matters which have been incorporated with the leather, through the use of extracts at high concentrations, giving yields in weight (rendement) appreciably higher than in ordinary leather.

The Italian Association for the Leather Commerce and Industry, always alive to the interests over which it has charge, has appointed a Commission to study this question, and the present writer, who has the honor to be on the Commission, considers it useful to submit to the Congress several considerations which he hopes will excite a detailed discussion.

The question whether a leather should be considered adulterated or not, is presented from two points of view, for we must establish:—

(1) If adulteration of leather should be considered to be confined to the presence of mineral matters, such as barium chloride, barium sulphate, magnesium sulphate, etc., fraudulently employed.

(2) If the adulteration should also be considered as due to the presence of an excess of organic matter: glucose, molasses, dextrine, etc., or even an excess of tannin incorporated in the leather for the sake of increasing the rendement.

As regards mineral substances such as barium chloride, magnesium sulphate, etc., which are commonly used for adulteration of leather, chemical analysis establishes that the presence of mineral matter (ash) above 2 per cent. should be considered as adulteration.

The official conditions for equipments for the French army limit the amount of mineral matter (as ash) to 1 per cent., whilst the conditions for the Belgium army limit it to 0.5 per cent., and the Italian army the limit is 2 per cent.

Whilst we admit the usefulness of these limits in guaranteeing a good quality of leather for military purposes, we wish to state that the so-called limits of mineral ash in leather, are not admissible as absolute terms, seeing that the presence of a certain percentage (which may amount to 3 per cent.) may be

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entirely due to the nature of the process of tanning, that is, may be due to natural causes such as the materials used for the decolorization of the tanning matters.

In view of the above considerations, and in order to establish definite limits, which shall preclude all discussion of the conditions in which leather shall be considered free from mineral matters and adulteration, we propose to fix the limit of permissible mineral ash at 3 per cent.

With regard to the question of an excess of organic matter in the leather, we should consider the question from the point of view of the presence of glucose, dextrine, etc., separately from that of the presence of an excess of tanning matter.

In the case of glucose or other sugary matters present in leather, 1.4 per cent., has been admitted as the maximum for commercial leather, but we must also consider that in many cases the currier employs glucose and dextrine in small proportions, for dressings, for lightening the color, and to give flexibility and brilliance to the grain; in this case it cannot be called adulteration, and the limit of glucose in leather so treated is 4 per cent. I consider therefore that the limit of 4 per cent. should be more widely admitted in commerce for commercial leather.

The question of the excess of tannin in leather, remains to be considered. In this case we must admit that up to the present, in spite of all the work that has been done on the subject, it has not been possible to assign definite limits to the amount of tanning matters which a commercial pure leather should contain, in proportion to the amount of hide substance which is combined with the tanning matters. It is on account of this that the only method we possess, and which is in general use in laboratories, is the determination of "water soluble matter." This method enables the chemist, up to a certain point, to determine by what method the leather has been tanned, for in a general way, one recognizes that leather treated by a rapid method of tannage, in which strong liquors have been given, yields higher percentages of water soluble matters. Nevertheless, it is exceedingly difficult to establish a limit for this amount of water soluble matter, in order to affirm that the excess above

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a prescribed percentage, should represent the amount of adulteration, because it often happens that a leather which has not been at all loaded with tanning matters, nevertheless yields on analysis a large quantity of water soluble matter.

In the same way it is not possible to determine if this excess of tanning matter is due to the direct tanning or to a retannage, which retannage cannot be legally considered as adulteration.

Summarizing these considerations, we propose to accept the following conditions:—

(1) That pure commercial leather, free from adulteration, must not contain more than 3 per cent. of mineral matter or ash.

(2) That leather yielding on analysis not more than 4 per cent. of glucose or dextrine shall be considered as leather free from adulteration.

THE NATURAL ACIDS OF THE TAN-LIQUORS AND THEIR INFLUENCE IN LEATHER MANUFACTURE.[1]

By R. Arnold Seymour Jones.

In the numerous methods which have been devised for the estimation of the acidity of yard liquors we have abundant evidence that the importance of this factor in the tanning process has long been recognized. After nearly thirty years' work we can estimate, more or less accurately, the so-called "acidity" of a tan-liquor, but whether we can and do interpret correctly the results when obtained is an entirely different matter. As has been shown in a recent paper by Professor Procter and the author (*J. S. C. I.*, December 15, 1910), there are at present about twenty methods which profess to estimate the "acidity" of tan-liquors, and they nearly all differ as to the results they give. In most cases, therefore, it would be a matter of some difficulty to determine exactly what useful information could be conveyed to the tanner. Consequently considerable confusion now exists as to what we require to estimate in this connection,

[1] From *Tanners' Year Book*, 1911.

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and it is the aim of this article to try to indicate how this confusion may be and is being reduced to order.

As we propose to advance into more or less unexplored territory it is advisable to determine how much information can be obtained by the means already at our disposal. We find that we can at present estimate:—

(a) The lime-dissolving power of the liquor by means of the Procter lime-water method.

(*b*) The plumping power of the liquor; roughly by—

(1) titration of a measured volume with standard alkali in a neutral atmosphere of petrol ether or coal gas, using congo red or methyl orange paper as an external indicator; or more accurately by—

(2) the new electrometric method of Law and Sand, whereby the "actual" hydrion concentration of the liquor is measured.

(*c*) The total acidity of the liquor by direct titration of a measured volume with standard alkali in a neutral atmosphere, using hæmatein or phenolphthalein paper as indicator.

(*d*) The nature of the acids in the liquor by complete organic analysis of the same.

Of these four pieces of information only one can at present be interpreted practically, and that is the lime-dissolving power. The plumping value of the liquor is also usually regarded as a piece of useful information, as it seems to be tacitly accepted that plumping assists tanning. But what evidence has ever been adduced to show that the swelling of the hide fiber will always assist the penetration of tannin? So far as public knowledge is concerned none has been brought forward, and it must be frankly admitted that the subject has received little attention from the tanner and less from the leather chemist; although it is probable that empirical facts have been deduced by thoughtful practical men, who have not considered it expedient to publish their results.

The question of the utility or otherwise of the swelling of the fiber indicates the main and most important question with regard to acids in tan-liquors, viz.: What are their functions and effects? About this the world at large at present knows nothing, and it is only recently that leather chemists have

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acquired sufficient courage to tackle one of the most complex and perplexing problems ever set to any technical chemist. In the autumn of 1909 von Schroeder published a paper entitled "Zur Kenntnis des Gerbprozesses," in which he devoted a little space to the question of the influence of acids during tanning; but his experiments were not very numerous, and it is impossible to generalize from them.

About three months previous to the publication of von Schroeder's work the author, in collaboration with Professor Procter, commenced to study the whole question, and since then much experimental work has been accomplished. The work is as yet unfinished, but it seems apparent that a true explanation of the role played by the acids will involve electrochemical colloidal theory of the most advanced type. Consequently it is not the intention in the present article to put forward any hypothesis, but merely to indicate the lines on which work is being done, and to deal very briefly with one or two aspects of the question.

Before proceeding further let us define what we mean by acids and acidity. In the aforementioned paper by Professor Procter and the author, and in an article by the former, (JOURNAL, Vol. VI, p. 445) the modern ionic conception of the nature of an acid is sufficiently clearly stated, and the lay reader is recommended to those articles for fuller information. For the purposes of this paper suffice it to state that we now regard acids as bodies which in aqueous solution split up to a greater or less extent into two sorts of extremely small particles or ions, the hydrogen which is present in all acids forming one species of little particles called the hydrion group, and the remainder of the acid molecule going to form the other kind of particles—the anion group. Whether these particles are more correctly portrayed as combined with water, *i.e.*, hydrated, is of no importance for our present purpose, for it has been found that the characteristic of an acid is the presence of more than a certain quantity of these hydrogen ions, and we thus have our first definition of an acid. This is not yet complete, however, for we find that the strongest alkali solutions have a definite, though extraordinarily minute,

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concentration of hydrogen ions. The opposite of the hydrion is the anion particle characteristic of all alkaline solutions, known as the hydroxylion, and consequently an acid solution may be defined as one in which the concentration of the former exceeds that of the latter. In neutral aqueous solutions the two are equal, hence the neutrality.

To turn to the experimental side, our first step was to make a few tentative experiments to determine what acids were present in normal tan-liquors in such amounts as to have any appreciable influence on the tanning process. We found, of course, that all acids present in any quantity weere of the organic series, and in the majority of the liquors examined the volatile fraction, chiefly acetic, propionic and butyric, was larger than the non-volatile gallic and lactic, acids. The five acids mentioned constitute the effective portion of the natural acids of the normal tan-liquor, and where the original material contains glucosides in any quantity the resulting fermentative actions may produce a very considerable acid concentration almost immediately after leaching. In fact, one of the difficulties we have encountered has been our inability to obtain neutral liquors from certain tanning materials. This, of course, raises the general question as to whether the tannins themselves may not be regarded as acids. Mr. A. G. Perkin, our leading English expert on the question of the chemistry of the tannins, has, however, stated that it is improbable that the catechol tannins possess carboxyl groups, *i.e.*, that they are not structurally acids. But as certain phenols produce a hydrion concentration, the possibility of certain tannins, which are phenolic bodies, behaving electro-chemically as acids remains, particularly among the pyrogallol series.

It will probably be shown that for a satisfactory reaction, whether physical or chemical, to take place between the hide fiber and a vegetable tanning material that a certain degree of acidity is necessary. The two practical questions which require answers are—

(*a*) Which acids accelerate and which retard the tanning process?

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(*b*) Does acid swelling lead to a larger or smaller ultimate absorption of tannin?

Our results so far have shown that it all depends on, firstly, the nature of the acid, and secondly, the nature of the tanning material. We have three reacting substances, viz., the hide fiber, the tannin, and the acid, and we may have three reactions, all of which probably take place in the liquor:—

(*a*) The action of the acid on the hide fiber.

(*b*) The action of the acid on the tannin.

(*c*) The action of the acid modified tannin on the acid modified hide fiber.

The first of these reactions is a very rapid one and is probably completed during the first few hours that the skin is immersed in the liquor. It has been extensively studied by Professor Procter, and the evidence seems overwhelmingly in favor of actual chemical combination taking place between the two. Before any tanning takes place, therefore, we get our hide fiber severely modified.

Of course, the mere swelling of the hide fiber has quite a considerable physical effect in the tanning process. If we take a piece of hide, plump it reasonably with an organic acid, and then tan it, and we take another similar piece and tan it as far as possible in the absence of acid, other conditions being equal, the first piece will be much fuller and thicker leather than the second. With mineral acids, however, the opposite effect is often produced and a thin starved leather results. Excess of organic acids will act in exactly the same way as mineral acids. We have found that if an acid swollen hide be placed in the first tanning liquor, which is not so acid as itself, that the tannin proceeds to expel the acid until ultimately practically none remains. For further details as to the action of acid on the hide fiber the reader is referred to Professor Procter's paper.

The second reaction which is sometimes hardly perceptible, especially with the weaker acids, is comparatively much slower, being a question of days. So far as I am aware the action of acids on tannin solutions has never been studied, and yet the point is so important that it now appears to be the

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key to the problem. In the cases of weak acids, like acetic and propionic, the action on the tannin is usually, but not always, nil or negligible, and these cases often coincide with increased absorption of tannin. With the stronger acids, on the contrary, the effect is so great as to modify the whole process, and as a rule the strong mineral acids are to be avoided for use in tan-liquors.

It is very interesting to note that the action of the acids in the tanning process is not directly attributable to the "strength" of the acid alone, *i.e.*, to its hydrion concentration, for the anion seems to play a great part. Certain anionic groups have the power of attaching themselves to the tannin molecule, and sometimes precipitation takes place. We thus necessarily complicate the problem, for we must differentiate the effects of the hydrion and anion, and it is within the bounds of possibility that we may have to attribute certain phenomena to the efforts of the undissociated acid molecule. It will be seen that this subject alone provides an enormous field of research.

Several observers have noticed that with very strong solutions of nearly all acids the precipitation of tannin by gelatine is prevented. Similarly certain acids in great concentration greatly hinder and ultimately stop the tanning process, this effect being particularly marked with the stronger mineral acids. This is probably due to a double effect; first, hydrolysis of the hide fiber; and secondly, the disruption of the tannin under the influence of too much acid.

When we have completely solved the problem of the acid action on the hide fiber and that of the acid action on the tannin, we may then turn with some hope of success to the elucidation of the action of the acid modified tannin on the acid modified hide fiber.

In speaking of the natural acids of the tan-liquors some years ago, the late Franz Kathreiner, whose knowledge of this subject was very deep, said, "Try to regard them as your friends." The advice is most sound, and in the presence of the acids is in most cases inevitable, why not utilize them? We are not yet doing so and we shall not be able to do so until we understand why and how they act.

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QUALITATIVE ANALYSIS OF TANNINS.[1]

By U. J. Thuau and P. De Korsak.

The increasing use of tanning extracts gives increasing importance to the problem of identification of the various tannins pure or mixed. H. R. Procter has published tables showing the colorations given by each tanning material with various reagents These colors are often nearly alike, so that in the case of some tannins it is sometimes difficult to distinguish one from another even when pure, and in the case of mixtures the color method is impossible of application.

Messrs. Stiasny and F. Jean have studied the action of formaldehyde and hydrochloric acid on the different tannins. This is actually the only exact method permitting the separation of the tannins into two great groups, the catechol and pyrogallol tannins; the former being entirely precipitated from their solutions by boiling with formaldehyde and hydrochloric acid, the latter but little or not at all.

To 50 cc. of tannin solution of analytical strength, are added 10 cc. of 40 per cent. formaldehyde and 10 cc. of hydrochloric acid. The whole is placed in an Erlenmeyer with reflux condenser and boiled 10 minutes. If the tannin is pure catechol, the precipitation is complete; if it is pure pyrogallol, the solution remains clear; if it is a mixture, the catechol tannin is precipitated and the pyrogallol remains in the clear solution. The filtrate is tested by pouring some into a test-tube and adding 1 or 2 grams of crystals of sodium acetate. On pouring in (without shaking) 1 cc. of a 1 per cent. solution of iron alum, a blue or violet color is obtained, more or less intense in proportion to the quantity of pyrogallol tannin present. The value of this reaction in detecting adulteration of pyrogallol tannins with catechol and vice versa, is evident.

The authors have repeated the experiments of Stiasny on the action of formaldehyde and hydrochloric acid on the various tannins, and confirmed his results. F. Jean claims that the precipitate, washed and dried at 105° C, determines by its weight the quantity of catechol tannin present in the solution.

[1] Abridged from *Le Cuir*, IV, p. 383.

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Stiasny however asserts that numerous experiments show that when this method is applied to mixtures of the two kinds of tannins, the precipitate entangles and carries down a part of the pyrogallol tannin. This statement of Stiasny is confirmed by the experience of the authors. They added to equal quantities of quebracho known amounts of chestnut extract. Since chestnut alone gives no precipitate with formaldehyde and hydrochloric acid, the quantities of the precipitate should be the same for each mixture as for the quebracho alone. This was not the case, but the weight of the precipitate was in some instances twice as great as that given by quebracho alone.

Three chestnut extracts were compared, one of which was decolorized with blood and one with carbonate of lead, the third being untreated. The last gave no precipitate with formaldehyde and hydrochloric acid. The extract treated with blood gave a slight turbidity, and that treated with carbonate of lead a considerable precipitate. Boiling for 10 minutes without addition of reagents produced no result. Boiling with hydrochloric acid alone gave almost the same results as when both reagents were employed. The authors suggest that the precipitate in the blood clarified extract was due to albumen, and in the other to tannin entangled by the chloride of lead.

The following extracts and other substances were examined:—

Pure chestnut, unclarified. No ppt.

Chestnut much clarified with $PbCO_3$. (Ppt. due to HCl alone.)

Chestnut much clarified with blood. (Ppt due to HCl.)

Pure oak. Small ppt. Filtrate contains tannin.

Crystallized sumac. (Ppt. due to HCl alone.)

Valonia. No ppt.

Solid extract of myrobalans.	No ppt. hot.
Extract of hulled myrobalans.	Slight ppt. on cooling.

Pure sulphited quebracho. Complete precipitation.

Mangrove. Complete precipitation.

Pure gallic acid. Partial precipitation.

Pure pyrogallic acid. Partial precipitation.

Pure pyrocatechin. Complete precipitation.

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The authors have discovered a method of detecting mangrove in quebracho, and even of estimating its quantity. Quebracho, treated with strong sulphuric acid and boiled is completely precipitated. The filtrate, strongly acidified with H_2SO_4 gives no reaction with 10 per cent. silver nitrate solution. Mangrove similarly treated gives a persistent white precipitate which settles very slowly. In mixtures of the two, the amount of precipitate is proportional to the quantity of mangrove present.

The authors have also studied the action of nitrate of silver in precipitating tannin, not only by boiling with sulphuric acid but also by acetate of lead, the excess of lead being thrown out with Na_2SO_4. In this case the action is much less distinct, the quebracho also giving a cloudiness. Several tanning materials were examined by both methods, results being given in the following table. Boiling with sulphuric acid and then treating with $AgNO_3$ is called method 1, and method 2 involves precipitation with lead acetate and removing excess of lead with Na_2SO_4 and then treating with $AgNO_3$.

Material	Method 1	Method 2
Quebracho	No ppt.	Cloudy
Mangrove	White ppt., finely divided	White ppt., finely divided
Oak.....	No ppt.	No. ppt.
Chestnut	No ppt.	No. ppt.
Valonia	Slight ppt.	No. ppt.
Sumac	Ppt.	Ppt.
Myrobalans	Ppt.	Ppt.
Gallic acid	Ppt.	Ppt.
Pyrogallic acid	Ppt.	Ppt.
Pyrocatechin.....	Ppt.	Ppt.

To sum up results on quebracho and chestnut:—If quebracho extract is only partially precipitated by formaldehyde and hydrochloric acid, it is adulterated with a pyrogallol tannin. If it is entirely precipitated, it is either pure or adulterated with another catechol tannin, *e,g.*, mangrove, whose presence may be shown by the nitrate of silver reaction.

If chestnut extract treated with formaldehyde and hydrochloric acid remains clear, it is either pure or mixed with another pyrogallol tannin, *e.g.*, myrobalans, sumac or valonia. If myrobalans is present there will be a precipitate on cooling.

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A further confirmation is found in the nitrate of silver precipitate. Sumac giving no precipitate with formaldehyde and hydrochloric acid, will be shown by giving a nitrate of silver precipitate by both methods. Valonia gives a slight precipitate by method 1, and none by method 2.

Care is necessary not to be misled by a precipitate which often appears in carrying out the sulphuric acid and silver nitrate test, at the moment when the $AgNO_3$ is added, but disappears on boiling. This is due to the crystallizing out of silver sulphate.

Extracts are often adulterated by the admixture of sulphite cellulose extract. This may be detected in quantities as small as 3 per cent. by the aniline reaction for cellulose.

CONTRIBUTION TO THE QUALITATIVE ANALYSIS OF TANNINS.[1]

By Dr. Leopold Pollak, Aussig.

I refer to the second part of the article by Thuau and de Korsak (page 523, this issue), describing a test of various tannins, especially distinguishing between mangrove and quebracho by means of silver nitrate. Since the two gentlemen say nothing about the nature of the silver precipitate, it will perhaps be appropriate to say something on that point.

I have during some years collected much material which may serve in detecting mangrove in extracts, and because I was actively concerned in the extract industry I had the best opportunity to test the method in all possible variations. The problem was to identify mangrove among other tanning materials by means of its higher content of chlorides. The mangrove takes up from the salt water in which it grows a large amount of chlorides, and these all pass into the extract in the process of manufacture. Quebracho contains only traces of chlorides, and myrobalans a small quantity. It would appear easy to develop both qualitative and quantitative tests for mangrove, but any extract maker will at once see that such a test will only apply where the method of manufacture of all the extracts compared

[1] *Collegium*, Sept. 2, 1911.

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is identical, for differences in the chlorine content of the water employed or the addition of hydrochloric acid in the sulphiting process would make the tests useless. Nevertheless I can identify mangrove by means of its chlorine content, taken in connection with other peculiarities which are known to me. Dr. Paessler has for about two years used my tables for research purposes at Freiberg. I only offer these observations to advise Messrs. Thuau and de Korsak that the white precipitate is simply a chlorine precipitate, as is easily proved. Therefore this reaction can only give partial results, and may in the hands of one not expert in extract manufacture lead to wholly false conclusions, and it can in no case be quantitative. All the tanning materials which according to Thuau and de Korsak give a precipitate with silver nitrate really contain chlorine in varying quantities. I cannot forbear in conclusion to warn in regard to this reaction every one not well acquainted with the various processes of extract manufacture, for chlorides are found almost everywhere.

THE THUAU AND DE KORSAK PROCESS FOR DETECTING MANGROVE IN TANNING EXTRACTS.[1]

By Dr. Louis Allen and Dr. Martin Auerbach, Hamburg.

The fact that the tannin of mangrove so closely resembles that of quebracho that by the ordinary tests it is not possible to distinguish the one when mixed with the other, has led to the adulteration of many commercial quebracho extracts with mangrove. The leather chemists of many lands have busied themselves to find reactions which would make it possible to distinguish these two materials in mixtures. Here and there these efforts have been crowned with success. But since each laboratory jealously guarded its secret, it came about that the results of any two laboratories failed to agree, and since the methods used were not comparable, each could neither confirm nor contradict the results of the other.

At the last international congress in Paris a commission was created for the testing and comparison of the various methods. This commission has not yet reported. Meanwhile, at the last

[1] *Collegium*, Sept. 16, 1911.

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meetings of the English, French and Austrian sections, methods for the detection of mangrove in quebracho were described. Of these, only that reported by Thuau and de Korsak in Paris has been published, and thus made available for comparison.

Because of the importance of the subject, we at once repeated the work of Thuau and de Korsak, at least in so far as it relates to the recognition of mangrove in quebracho extract, and can confirm their observations. It has occurred to us that since this reaction depends on the presence of chlorides we may simplify the process considerably by using the ash of the extract, or better to examine the total solids obtained by analysis and then apply the silver nitrate test.

Some years ago it was shown in this laboratory in the examination of a lot of mangrove for sea-damage that mangrove contains much chlorides. The idea naturally presented itself that this fact might be used for distinguishing between mangrove and quebracho. On a little reflection the idea was given up because the use of natural waters in the manufacture of extracts must introduce more or less chlorine into them.

An extract consisting of mixed mangrove and quebracho was treated with sulphuric acid and then ashed and ignited to complete destruction of organic matter. A part of the same was neutralized with soda and then ashed and ignited. The first portion showed no silver nitrate reaction, since the hydrochloric acid had all been expelled by the sulphuric acid. The second portion gave a precipitate, soluble in ammonia and reprecipitated by nitric acid.

We then prepared a quebracho extract with distilled water, and one with tap-water. In the first the Thuau-de Korsak reaction failed, in the second it was plainly visible. It would appear that Messrs. Thuau and de Korsak had worked with extracts which they themselves had prepared. We have tested a guaranteed pure quebracho extract by their method and found a positive result from their reaction. Finally we have examined a mixed mangrove and quebracho extract which gave the reaction, but after boiling with sulphuric acid failed to give it in spite of the presence of mangrove. Since therefore the reaction depends on the presence of chlorides, the addition of salt to an extract makes the method deceptive.

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ABSTRACTS.

Lactic Acid Analysis. W. KLAPPRORH. *Chemiker Zeitung,* 1911, No. 112, pp. 1026-7.—Messrs. Besson,[1] Monin[2] and Sunder[3] have lately undertaken a thorough examination of lactic acid analysis.

Besson,[4] whose work is most important shows that the anhydrid content, and therefore the total acid content formed by the old methods was too high. The lactic acid was boiled with an excess of sodium hydroxide, and the boiling alkali acted upon the sugar and dextrine contained in the ordinary commercial lactic acid to form substances having an acid reaction. So in the following titration a smaller quantity of N/1 H_2SO_4 is used up than corresponds to the anhydrid. The solution should also only be allowed to come to a boil.

In the laboratory at Freiberg a method arranged by the author is used. It has a few modifications of the Besson method—namely—after the titration of the free acid instead of allowing the solution containing an excess of NaOH to stand in the cold, it is warmed, since it hastens the conversion of the anhydrid and does not have the bad effect of boiling. It was found better also to take careful account of the excess of H_2SO_4, since it was found by experiment that a greater addition gave a less total acid content. The advisability of the use of H_2SO_4 is itself doubtful because in boiling it tends to make a part of the lactic acid back into an hydrid. Warming works well, also in this case.

In the laboratory of C. H. Boehringer and Son it has also been discovered that it is unnecessary to use 100 cc. portions of acid—for 10 cc. portions are very satisfactory. This applies for private laboratory experiments but if the results of different chemists are to agree the fluid must be weighed.

After consideration of the above mentioned facts the laboratories which made the experiment agreed on the following method for examination of lactic acid. Weigh out 1 gram of the acid in question and dilute in a small beaker with about 20 cc. distilled water. Titrate this solution with normal NaOH (as free as possible from CO_2), using phenolphthalein as indicator, until it is a permanent red. Then if the acid is of medium concentration add exactly 1 cc. of NaOH, which will have its effect immediately. If the acid is of high concentration add 3 cc. of NaOH and warm on a boiling water-bath five minutes. Then retitrate with H_2SO_4 normal and after the color change add 1 cc. in excess. Warm two minutes on the water-bath, and finish titrating with N/1 NaOH.

The number of cc. of NaOH used in the first titration multiplied by nine gives the content of the lactic acid in free acid, that is lactic

[1] Information from the Laboratory of C. H. Boehringer & Son, Lower Ingelheim on the Rhine.

[2] Révue génerale des Matières Color, 1911, p. 279.

[3] *Ibid.*, 1910, p. 312.

[4] See abstr., this JOURNAL, v, 231, and vi, 321.

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acid + ½ lactic acid anhydrid. Then the total amount of NaOH used minus the number of cc. of H_2SO_4 used and multiplied by nine gives the total acid content. E. A. B.

Criticism on the Analysis of Tannin Extracts. Address by M. E. Roy, Assembly of Syndicate of Tanning and Dyestuff Extract Manufacturers of France. *La Halle aux cuirs,* 1911, 257-8.—The speakers theme is the inadequacy of chemical analysis to measure the practical value of these materials. Tannin is not a definite uniform substance, but may exist in innumerable modifications which vary in their effect upon hide. A wood extract of specified tannin content and color may be blended with cheaper materials rich in tannin, such as myrobalans, or with sulphite pine lyes and still satisfy all the requirements of analysis. Numberless mixtures of this sort can be made which the chemist cannot detect. Another element which affects the interpretation of the tannin analysis, is the method of extraction used by the maker, whether cold or hot, the degree of desiccation of the raw material, etc. Here the influence of the non-tans is held to be paramount, but this is not precisely defined nor rendered by analysis. As to colorimetric examination of extracts, it often transpires in practice that there is little relation between the color of an extract and that it gives the leather. In conclusion, the extract maker, while admitting that chemical analysis may afford a relative protection against fraud and serve to compare products of the same manufacture, refuses to recognize the chemist as an infallible judge of the efficient value of extracts. W. J. K.

Tannage with Bromine and Hypobromites. L. Meunier and A. Seyewetz. *Collegium,* 1911, 289-91.—The insolubilization of gelatine by bromine has been earlier referred to by the authors (*Monit. sci.,* 1909, 31) and offers another example of tannage through oxidation. If gelatine previously softened in water be treated 2-3 hours with bromine water containing 15 grams per liter and then thoroughly washed, it is found to be insoluble in boiling water. Trials with 10 grams portions of dry gelatine treated with varying amounts of bromine water for 3 hours followed 48 hours washing in a flask, gave following amounts of bromine retained in the product:

Grams water	450	300	200	200
Grams satd. bromine water	50	100	300	300
Per cent. bromine (dry gelatine=100)	0.46	0.89	1.96	2.40

A more thorough washing or treatment with sod. bisulphite reduced the bromine retained to 0.90 per cent. which amount seems necessary to effect insolubilizations.

In experiments on hide, to avoid the annoyance from excessive swelling caused by considerable amounts of hydrobromic acid inevitably present, salt was added. For 1 kg. white pelt in 2 liters water with 100 grams salt, 2-3 liters bromine water (20 grams per liter) were gradually added. After thorough washing in water for 1-2 days, or rapidly with

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bisulphite, a pure white leather is obtained, absolutely imputrescible and fairly resistant to hot water although not equally so to quinoned hide.

Owing to the slight amount of tanning material fixed, the hide fiber, especially in the grain, is very fine. Any other tannage, chrome, tannin, alum, etc., may be superimposed. The authors intend to study tannage with chlorine which would appear to have commercial possibilities.

W. J. K.

The Action of Light in Tanning, Especially in the Chrome Process. Address to the Austrian Leather Industry Chemists. B. KOHNSTEIN. *Collegium,* 1911, 291-6.—The speaker enumerates miscellaneous instances of the darkening or bleaching of leather through exposure to the light during manufacture. In chrome tannage, it is necessary to immediately protect from light the leather coming from the first bath, to prevent darkening, especially when the product is not intended for black leather. The necessity for this precaution, the speaker demonstrates with samples of leather prepared as follows: Small pieces of pelt are pickled, then treated with 5 per cent. $K_2Cr_2O_7$, 2½ per cent. HCl, 120 per cent. water, then stretched on a board, covered with open woven textile and exposed to the sunlight for ½ to 2 hours. It is then found on examination with a lens that the illuminated portions are matt while the rest has the natural polish in relief. The action of the chemically active light rays is further shown by exposing similarly chromed hide under colored glasses with dark red and yellow glass there is little action. The effect in general, is analogous to that obtained in photography by the carbon process; by action of light, the chromed gelatine becomes insoluble. According to H. Meyer, the reaction is

$$K_2Cr_2O_7 = Cr_2O_3 + K_2O + 3O.$$
$$K_2O + K_2Cr_2O_7 = 2K_2Cr_2O_7.$$

the Cr_2O_3 being absorbed, rendering the gelatine insoluble. Eder showed that the liberated oxygen escapes. W. J. K.

The Preservation and Disinfection and a New Method of Anthrax Sterilization. (Address) B. KOHNSTEIN. *Collegium,* 1911, 297-304.—Hides are preserved by (1) dehydration by drying or addition of dehydrating salts (2) antiseptics (3) cooling. Some of these agents, however, may lessen the value of the hide for leather making. Poor ventilation during drying occasions "dry-rot" especially in Java buffalo hides. Too high temperature produces glue, or coagulates the blood giving discoloration. Exposure to smoke in drying tans the hide prematurely. Frozen hides give loose leather. Many dehydrating salts are unsuitable; anhydrous sod. sulphate or alum withdraw water vigorously but the heat generated curdles the blood and also produces glue. Alum in addition tans the hide and most organic antiseptics have the same action, for example, carbolic acid, formaldehyde and picric acid. Salt is the best and cheapest preservative; previously used salt is not suited. Blue, red and

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rusty spots marbled on the grain result from insufficient salting. Many of the substances used for denaturing salt reduce its dehydrating action; when petroleum oils are used for this purpose, spots are frequent. The products of putrefaction in the hide cause a brown precipitation with the iron of the hämoglobin of the blood. The speaker has found a good preventive in formic acid which is antiseptic and without tanning action. Another suitable denaturing agent would be found in butyric acid containing naphthalene in solution.

After discussing anthrax infection, the substances used for its sterilization are referred to. Mercuric chloride is expensive, poisonous and very difficult to wash out from the pelt. It is prone to react with the sulphide of the limes or the natural sulphur of the hair which is objectionable except for black leather. In union with the hygienic institute of the University of Vienna, the speaker has perfected a satisfactory method which employs 2 per cent. HCl, 10 per cent. salt. W. J. K.

Notes in Reply to Queries Concerning Mixed Tannage of Glazed Leather. *Le Cuir,* 1911, (4) 574-5.—The liquors used in the suspender vats, especially when prepared from quebracho, give a deposit or slime which prevents the penetration of the tannin. Special apparatus may be used for filtration, filter presses, etc., or the turbid liquor may be filtered through fresh material. Or to avoid loss of tannin, filtration may be dispensed with through agitation of the liquors in the vats by suitable machinery. Three methods of suspension are used: over sticks either lengthwise or breadthwise, or else from hooks for the entire length. The situation of the tannery often determines which is employed, the last method requiring deep pits while the others demand greater extension of space. It is advisable to crop the hides directly on leaving the handlers for the sake of economy. The trimmings, being of less value do not merit a tannage with such expensive materials as oak bark. The flanks may be finished by drumming 24 hours in a liquor of 15° Bè, letting lie piled 20-24 hours, then rinsing in weak liquor. If high rendement is required, they may be re-tanned in a special extract. In completing the regular tannage in the pits, the necks are given half the time of the butts. W. J. K.

The Tanning and Currying of Satin Calf. H. P.....*Gerber-Courier,* 1911, [52] No. 37.—The light or medium weight dried hides are taken daily from the soaks, particularly in summer, and replaced in fresh water. After two days they are stretched, again placed in fresh water and let stand till next day. Liming begins with an old liquor to which some fresh lime has been added. The hides are turned daily in the lines which are bettered every 2 days; 8-10 days are usually required. After unhairing, liming is continued if the hide is not entirely soft. A bran drench is used at 32-33° C. until the hides float. The tanning materials are pine, oak and sumac, best combined. After 4-5 vats, the hides are broken and fleshed and then the main tannage is carried out in the drum, consisting of a combined sumac tannage and chamoisage. A

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sumac liquor of 3-4° B. is mixed with pure whale oil (⅛ liter per hide) and milled with the hides for 9-10 hours, whereby considerable heat is generated. The hides are then piled and covered and let stand with advantage as long as over-heating may be risked. After washing, greasing with degras, the blackening and further finishing are as usual.

W. J. K.

Glaze for White Leather. *Ledertechn. Rundschau,* 1911, 283-4.—This is much more difficult to secure than with vegetable tanned leather, especially after the leather is worked into shape; this is due to the porosity of tawed leather which rapidly absorbs the dressing. A specially suited composition is made by soaking linseed with 4-5 times its weight of cold water for several hours, then boiling for one hour with vigorous stirring. On cooling, the product is strained through coarse linen into an enameled vessel in which it is warmed and meanwhile shaved grain soap is stirred in and dissolved. A test sample on cooling should be a thin jelly and opalescent if the right amount of soap is present. One egg yolk to every liter is next stirred in. The dressing is applied to the carefully cleaned leather with a soft sponge and when dry is rubbed with flannel. With entire hides, machine rolls may be used.

W. J. K.

Salted Hides. *Gerber-Courier,* June 24 and July 1, 1911.—A defect to which salted hides are liable consists of holes as large as a pin-head, (*Salzstippe* or *Salzpiquer*) penetrating deeply into the grain. These owe their origin to the fact that the hide was beginning to decay before it was salted. The salt stops the decay, but causes the hide-substance which had begun to decay to dissolve out. Salt-stains are due directly to filth clinging to the hide, sweat, blood, dung, earth, etc. They are also caused by the hides coming in contact with iron, coal, etc., during transportation and unloading, and also by the hide becoming dry in spots by exposure to the sun or a current of air. Salt-stains may also be caused by substances used to denature the salt, such as fish-oil, tar, tobacco-dust and red chalk. Pure salt cannot cause stains, but by softening the grain it makes it easier for coloring matters to penetrate. The use of soda or soap powder for denaturing salt is very objectionable, as they act energetically on the hide-substance and by their alkaline properties darken the color of the adherent substances and cause them to make darker stains. Volatile mineral oils are very satisfactory substances for denaturing salt. Only ¼ per cent. is necessary and they do not injure the hides in any way. Small spots softer than the rest of the hide and dull in color are often noticed, due to impurities in the salt. If, for instance, the salt contains small stones, each stone prevents a small spot from being salted promptly and thus becomes a center of partial decay.

Aids in the prevention of salt-stains are:—. Cleansing of the hides from dung, etc., before salting. 2. Salting of the hides as promptly as possible after flaying, especially in warm weather. 3. Salting on the

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flesh side, and not piling too high. 4. Avoidance of harmful denaturing substances. 5. Protection of salted hides from drying, and proper placing and handling during storage. 6. Not to buy hides which have been long stored.

The writer recommends the following procedure:—Soak 1-3 hours in water, thorough cleansing. Drain. Spread on clean floor hair down. Apply salt, 8-10 per cent. of the wt. of hide, carefully spread. Fold up carefully. Pile in a water-tight tank. If the brine flowing out from the hides does not cover the piled hides, add enough 15 per cent. salt solution to cover. After 5-7 weeks in this pickle, take out and drain. Salt again lightly on the hair side, and pile in a cool room.

L. A. C.

Wattle Bark; Utilization of——. *Bull. Imp. Inst.*, 1911, 9, 116-121.—The cultivation of wattle-trees is being extended in Natal, Transvaal, and in British and German East Africa. In British East Africa the plantations have reached the stage at which bark production can be commenced, and a small consignment has been recently placed on the London market. The exports of wattle bark, chiefly to Germany, for the four years, 1906-1909, from Natal, Cape Province, and Australia, were:—

	Natal		Cape province		Australian Commonwealth[1]	
	Weight cwt.	Value £	Weight cwt.	Value £	Weight cwt.	Value £
1906.....	295,130	89,056	1,437	318	431,896	162,453
1907.....	476,786	136,873	9,616	2,514	358,167	132,342
1908.....	491,748	133,510	5,233	1,053	260,364	102,510
1909.....	705,848	192,950	9,572	1,746	—	—

Among the advantages of wattle bark as a tanning material are that it varies very little in quality as marketed; it is rich in tannin, which can be easily extracted; and it is cheaper than other materials of similar quality and properties (compare Paessler, this J., 1911, 499). In the following table are given analyses of barks from British Territory which are now on the market or may be so in the near future:—

Name	Source	Tannin per cent.	Non-tannins per cent.	Ash per cent.	Moisture per cent.
Black wattle bark.....	Natal	35.2–39.8	7.3–10.3	1.5–2.8	9.5–11.7
Black wattle bark.....	Cape Province	40.1–44.1	7.1–13.0	1.5–1.8	10.1–10.9
Black wattle bark.....	British E. Africa	36.7–42.1	9.4–12.7	1.5–2.4	10.2–13.0
Black wattle bark.....	Australia	38.3	4.4	—	11.1
Golden wattle bark.....	S. Australia	40.2–49.5	9.0–9.4	—	11.2

Samples of wattle-bark, with specimens of leather tanned with them, can be seen at the Imperial Institute.—A. S. (from *J. S. C. I.*).

[1] These figures are for "tanning materials" and may include some mallet bark.

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PATENTS.

Evaporating Apparatus. U. S. Patents No. 1,003,912 and No. 1,005,553. PAUL KESTNER, Lille, France.

Process of Preparing Desiccated Vegetable Extracts. U. S. Patent No. 1,005,554. PAUL KESTNER, Lille, France.

The extract is caused, after reaching a high state of concentration, to traverse in thin sheets a space heated above 100° C., and then is discharged into a high vacuum, whereby a substantially solid, dry and porous extract is obtained.

Evaporator. U. S. Patent No. 1,005,571. JOHN PARKER, Philadelphia.

Evaporating Apparatus. U. S. Patent No. 1,005,600. GEORGE WESLEY CHILDS, Ridgway, Pa.

This is the form of evaporator, in which four or any other number of effects are so arranged that any one may be the first effect. By using the pans in rotation, the coating which tends to form on the inner surface in the later effects is dissolved off by the low density liquid of the first effect.

Table for Setting Out Leather. U. S. Patent No. 1,003,529. JAMES T. SMITH, Newark, N. J.

Machine for Measuring the Area of Leather and the Like. U. S. Patent No. 1,003,850. WILHELM ADOLF WÜST, Frankfort on-the-Main, Germany, Assignor to Moenus Machine Works.

Process and Product for Use in Unliming Hides and the Like. U. S. Patent No. 1,006,539. GUSTAV EBERLE, Stuttgart, Germany.

This is one of the so-called enzyme bates, and contains bile, extract of intestinal mucus and extract of the pancreas. The finished product, it is claimed, is a solvent of grease and lime soaps.

Process for Decolorizing Tanning Extracts. U. S. Patent No. 1,006,977. JOHANNES PAESSLER, FREIBERG and HEINRICH ARNOLDI, Weinheim, Germany.

The process involves treatment with aluminum amalgam, previous to concentration.

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Journal of the

American Leather Chemists Association

Vol. VI DECEMBER, 1911 No. 12

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members. $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

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EIGHTH ANNUAL MEETING.

The eighth annual meeting of the Americal Leather Chemists Association will be held at Washington, D. C., December 7, 8 and 9, 1911. The committee having in charge the arrangements for the meeting has selected the Hotel Raleigh, Pennsylvania Ave. and 12th St. as the place of meeting. A suitable room has

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been reserved for the meetings, and members who desire to retain rooms at the hotel are requested to apply directly to the management. The following is the schedule of prices:—Single rooms, $2.00 per day and up; with bath, $3.00 per day and up; double rooms, $3.00 per day and up; with bath, $4.00 per day and up.

PROGRAM.

THURSDAY, DECEMBER 7TH.

Morning Session:—

Opening remarks by the President.
Report of the Secretary-Treasurer.
Committee reports.

Afternoon Session:—

Address by Mr. E. C. Alsop, "Purification of Liquid Tannery Waste by Forced Oxidation."
Address by Mr. A. W. Hoppenstedt, "Seal Oil."
Address by Mr. Geo. A. Kerr, "Notes on the Acids and Acid Forming Value of Chestnut Wood and Chestnut Oak Bark Liquors and Extracts."
Address by Mr. H. C. Merrill, "Colors and their Application to Leather."

FRIDAY, DECEMBER, 8TH.

Morning Session:—

Committee reports.
Address by Mr. C. R. Oberfell, "The Composition of Leather from Different Parts of the Hide and the Importance of a Proper Sample for Analysis."
Address by Mr. John H. Yocum, "The Characteristics and Commercial Adaptability of Hides.

Afternoon Session:—

Address by Mr. A. H. Lockwood, "The Development of the Leather Industry in Relation to the World's Hide Supply."
Address by Wm. M. Norris, "Chrome Methods."
Address by Mr. Henry W. Healy, "Are Tanners Teaching Their Superintendents How to Think?"

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SATURDAY, DECEMBER 10TH.

Morning Session:—

Address by Mr. A. W. Hoppenstedt, "The Tannins."

Address by Mr. Alan A. Claflin, "The Tanning Properties of Waste Pulp Mill Liquors."

Election of Officers.

General Business.

Communications will be read from Prof. H. R. Procter and M. C. Lamb.

A paper is expected from Louis T. Roenitz on "The Preparation of Lime for Tanner's Use."

VALUE OF SULPHITE-CELLULOSE EXTRACTS FOR BLENDING.

By John H. Yocum and Thomas A. Faust

The use of the waste liquors from those paper mills employing the sulphite process for tanning purposes, has greatly increased during the past few years. Several methods of treating the raw liquor have been evolved, but none have brought this material strictly on a par with the standard tanning materials. Hides tanned alone with the sulphite-cellulose extracts have produced leather with a more or less tinny feel, often a harsh grain, and with the general appearance of not having been thoroughly tanned.

Most tanners who are using sulphite-cellulose extracts today, use them in conjunction with other tanning materials in varying proportions. Many have had a sad experience by blending, either due to the method of admixture of the tanning material with sulphite-cellulose extract, or to the particular tanning material used in conjunction with the sulphite-cellulose extract.

In regard to the former difficulty, the method which has given the greatest satisfaction is to dissolve each material separately, and run the hot solutions into the same tank, mixing and allowing to cool gradually.

A peculiarity of sulphite-cellulose extracts is the fact that they behave differently with the different tanning materials.

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The authors herewith present figures, showing the results of laboratory experiments in mixing sulphite-cellulose extracts with various tanning materials in varying proportions, percentages being based on the tannin content of the materials employed. The sulphite-cellulose extract used was one of the commercial products on the market. In each case, an analysis was made of the resulting extract, and the theoretical analysis was calculated from the tannin per cent. of the materials employed in the proportions in which they were used. Conditions in the tannery were followed as closely as possible in the mixing.

While these figures are merely the results of laboratory experiments and may vary more or less in practise, yet we think they may be of some value to the tanner who is interested in sulphite-cellulose extract. We do not believe that there is a great deal of variation in the different extracts of this type, that are on the market to-day, and these experiments probably apply to most of them.

Tables No. 1 and No. 2 show the results of the mixtures of two different samples of ordinary quebracho and two different samples of sulphite-cellulose extract. While the sulphite-cellulose extract is practically the same, the quebracho is a little different, the extract marked "B" being higher in moisture and lower in tannin than the one marked "A." You will note that there is a loss in tannin by the mixture of these two materials, the loss being calculated by deducting the percentage of tannin as actually found in the resulting extract from the tannin calculated as we mentioned above. The loss increases in proportion to the increased percentage of the sulphite-cellulose extract used. The loss in tannin in Table No. 2, where 30 per cent. of sulphite-cellulose extract and 70 per cent. of quebracho are used, is not as high as in Table No. 1 where the same proportions are used. This may be due to the quebracho extract, it being from two entirely different factories.

Tables No. 3 and No. 4 show the results of mixtures of two samples of liquid quebracho and two different samples of sulphite-cellulose extract. These liquid quebracho extracts are similar in character, having been chemically treated, and you will note that the analyses in the two tables are concordant.

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TABLE No. 1.—Mixture of Ordinary Quebracho "A" with Sulphite-Cellulose Extract "A."

	Sulphite-cellulose extract	Quebracho extract	10% sulphite-cellulose 90% quebracho		20% sulphite-cellulose 80% quebracho		30% sulphite-cellulose 70% quebracho		40% sulphite-cellulose 60% quebracho		50% sulphite-cellulose 50% quebracho	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture	49.05	21.72	24.05	24.50	27.46	27.23	30.20	29.88	32.23	32.66	35.07	35.34
Total solids	50.95	78.28	75.95	75.50	72.54	72.77	69.80	70.12	67.77	67.34	64.93	64.66
Soluble solids	50.69	74.15	70.03	71.77	65.67	69.42	62.92	67.15	59.67	64.76	56.82	62.47
Insolubles	0.26	4.13	5.92	3.73	6.87	3.35	6.88	2.97	8.10	2.58	8.11	2.19
Non-tannins	23.97	6.72	8.37	8.47	9.62	10.19	10.79	11.91	11.76	13.62	14.06	15.36
Tannin	26.72	67.43	61.66	63.30	56.05	59.23	52.13	55.24	47.91	51.14	42.76	47.11
Gain or Loss				—1.64		—3.18		—3.11		—3.23		—4.35

TABLE No. 2.—Mixture of Ordinary Quebracho "B" and Sulphite-Cellulose Extract "B."

	Sulphite-cellulose extract	Quebracho extract	10% sulphite-cellulose 90% quebracho		20% sulphite-cellulose 80% quebracho		30% sulphite-cellulose 70% quebracho	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture	50.56	25.87	28.90	28.35	30.62	30.81	32.52	33.28
Total solids	49.44	74.13	71.10	71.65	69.38	69.19	67.48	66.72
Soluble solids	49.42	68.78	65.16	66.84	62.51	64.91	60.54	62.97
Insolubles	0.02	5.35	5.94	4.81	6.87	4.28	6.94	3.75
Non-tannins	22.94	5.28	6.88	7.04	8.27	8.81	10.09	10.58
Tannin	26.48	63.50	58.28	59.80	54.24	56.10	50.45	52.39
Gain or loss				—1.52		—1.86		—0.94

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TABLE NO. 3.—MIXTURE OF LIQUID QUEBRACHO "A" AND SULPHITE-CELLULOSE EXTRACT "A."

	Sulphite-cellulose extract	Liquid quebracho	10% sulphite-cellulose 90% quebracho		20% sulphite-cellulose 80% quebracho		30% sulphite-cellulose 70% quebracho		40% sulphite-cellulose 60% quebracho		50% sulphite-cellulose 50% quebracho	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture	49.05	53.52	52.97	53.06	52.41	52.58	52.09	52.18	51.99	51.76	51.78	51.24
Total solids	50.95	46.48	47.03	46.94	47.59	47.41	47.91	47.82	48.01	48.24	48.22	48.76
Soluble solids	50.69	46.25	46.21	46.69	46.91	47.18	47.17	47.60	47.40	48.00	47.75	48.52
Insolubles	0.26	0.23	0.82	0.25	0.68	0.23	0.74	0.22	0.61	0.24	0.47	0.24
Non-tannins	23.97	7.00	8.66	8.70	9.92	10.41	11.40	12.02	13.06	13.85	14.15	15.53
Tannin	26.72	39.25	37.55	37.99	36.99	36.77	35.77	35.58	34.44	34.15	33.60	32.99
Gain or loss				−0.44		+0.22		+0.19		+0.19		+0.61

TABLE NO. 4.—MIXTURE OF LIQUID QUEBRACHO "B" AND SULPHITE-CELLULOSE EXTRACT "B."

	Sulphite-cellulose extract	Liquid quebracho	10% sulphite-cellulose 90% quebracho		20% sulphite-cellulose 80% quebracho		30% sulphite-cellulose 70% quebracho		40% sulphite-cellulose 60% quebracho		50% sulphite-cellulose 50% quebracho	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Twaddell	54°	40½°										
Moisture	50.56	55.06	54.63	54.62	54.07	54.10	53.57	53.73	53.18	53.24	52.61	52.80
Total solids	49.44	44.94	45.37	45.38	45.93	45.90	46.43	46.27	46.82	46.76	47.39	47.20
Soluble solids	49.42	44.71	45.18	45.17	45.59	45.71	45.90	46.10	46.40	46.61	47.13	47.08
Insolubles	0.02	0.23	0.19	0.21	0.34	0.19	0.53	0.17	0.42	0.15	0.26	0.12
Non-tannins	22.94	6.46	7.94	8.13	9.53	9.89	10.68	11.35	12.33	13.05	13.92	14.75
Tannin	26.48	38.25	37.24	37.04	36.06	35.82	35.22	34.75	34.07	33.56	33.21	32.33
Gain or loss				+0.20		+0.24		+0.47		+0.51		+0.88

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TABLE 5.—MIXTURE OF CUTCH AND SULPHITE-CELLULOSE EXTRACT "A."

	Sulphite-cellulose extract	Cutch extract	10% sulphite-cellulose 90% cutch		20% sulphite-cellulose 80% cutch		30% sulphite-cellulose 70% cutch		40% sulphite-cellulose 60% cutch		50% sulphite-cellulose 50% cutch	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture.....	49.05	28.02	29.68	30.42	32.47	32.23	35.10	34.76	37.04	36.35	38.93	38.27
Total solids	50.95	71.98	70.32	69.58	67.53	67.77	64.90	65.24	62.96	63.65	61.07	61.63
Soluble solids ..	50.69	71.12	69.37	69.07	67.08	67.03	64.15	64.57	59.40	63.03	52.93	61.06
Insolubles	0.26	0.86	0.95	0.51	0.45	0.74	0.75	0.67	3.56	0.62	8.14	0.57
Non-tannins....	23.97	19.97	20.35	20.37	21.12	20.77	21.29	21.28	21.14	21.60	21.48	22.05
Tannins.....	26.72	51.15	49.02	48.70	45.96	46.26	42.86	43.29	38.26	41.43	31.45	39.01
Gain or loss				+0.32		—0.30		—0.43		—3.17		—7.56

TABLE 6.—MIXTURE OF CHESTNUT EXTRACT AND SULPHITE-CELLULOSE EXTRACT "B."

	Sulphite-cellulose extract	Chestnut extract	10% sulphite-cellulose 90% chestnut		20% sulphite-cellulose 80% chestnut		30% sulphite-cellulose 70% chestnut		40% sulphite-cellulose 60% chestnut		50% sulphite-cellulose 50% chestnut	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Twaddell.....	54°	43°										
Moisture.....	50.56	58.37	57.70	57.60	57.05	56.80	56.13	55.96	55.21	55.36	54.31	54.47
Total solids	49.44	41.63	42.30	42.40	42.95	43.20	43.87	44.04	44.79	44.64	45.69	45.53
Soluble solids...	49.42	41.26	42.26	42.08	40.84	42.91	39.74	43.78	38.70	44.41	38.24	45.33
Insolubles	0.02	0.37	0.04	0.32	2.11	0.29	4.13	0.26	6.09	0.23	7.45	0.20
Non-tannins	22.94	13.26	14.35	14.23	14.62	15.21	15.21	16.25	16.14	17.07	17.12	18.09
Tannin.....	26.48	28.00	27.91	27.85	26.22	27.70	24.53	27.53	22.56	27.34	21.12	27.24
Gain or loss....				+0.06		—1.48		—3.00		—4.78		—6.12

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TABLE 7.—MIXTURE OF MYROBALANS EXTRACT AND SULPHITE-CELLULOSE EXTRACT "B."

	Sulphite-cellulose extract	Myrobalans extract	10% sulphite-cellulose 90% myrobalans		20% sulphite-cellulose 80% myrobalans		30% sulphite-cellulose 70% myrobalans	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture	50.56	13.43	18.05	17.15	22.98	20.86	27.78	24.58
Total solids	49.44	86.57	81.95	82.85	77.02	79.14	72.22	75.42
Soluble solids	49.42	84.58	77.10	81.06	73.96	77.55	69.20	74.03
Insolubles	0.02	1.99	4.85	1.79	3.06	1.59	3.02	1.39
Non-tannins	22.94	32.76	30.70	31.78	29.84	30.80	28.41	29.81
Tannin	26.48	51.82	46.40	49.28	44.12	46.75	40.79	44.22
Gain or loss				—2.88		—2.63		—3.43

TABLE 8.—MIXTURE OF VALONIA AND SULPHITE-CELLULOSE EXTRACT "B."

	Sulphite-cellulose extract	Valonia extract	10% sulphite-cellulose 90% valonia		20% sulphite-cellulose 80% valonia		30% sulphite-cellulose 70% valonia	
			Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Moisture	50.56	8.35	11.93	12.57	16.26	16.79	21.09	21.01
Total solids	49.44	91.65	88.07	87.43	83.74	83.21	78.91	78.99
Soluble solids	49.42	90.13	83.94	87.06	79.93	81.94	75.27	77.92
Insolubles	0.02	1.52	4.13	1.37	3.81	1.27	3.64	1.07
Non-tannins	22.94	25.46	25.16	25.21	25.07	24.95	24.35	24.70
Tannin	26.48	64.67	58.78	60.85	54.86	56.99	50.92	53.22
Gain or loss				—2.07		—2.13		—2.30

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This is the only case in which no loss of tannin was produced by the mixture of the ordinary tanning materials with the sulphite-cellulose extracts; in fact the tannin as actually found was slightly higher than the theoretical amount.

Table No. 5 shows the results of mixtures of mangrove cutch and sulphite-cellulose extract, and shows practically no loss of tannin until more than 30 per cent. of sulphite-cellulose extract is used in the mixtures. Where half and half is used, there is a loss of 7½ per cent. of tannin as against the theoretical amount.

Table No. 6 shows the mixtures of chestnut and sulphite-cellulose extract. In this case, the greater the percentage of sulphite-cellulose extract, the greater the loss in tannin, it amounting to a considerable loss where 30 or 40 per cent. of sulphite-cellulose extract is used.

Table No. 7 shows the mixtures of myrobalans and sulphite-cellulose extract, and again we find a considerable loss in tannin as against the theoretical amount.

Table No. 8 shows the mixtures of valonia and sulphite-cellulose extract. These results do not show as great a loss in tannin as mixtures of myrobalans and sulphite-cellulose extract.

Thus with the exception of liquid quebracho, there is a greater or lesser loss of tannin by such mixing, the amount varying according to the material used.

From the few analyses that we have made, it would appear at first sight as if the pyrogallol tannins showed a greater loss than the catechol, although cutch would be an exception to this; however, this would not be borne out by a closer examination.

Color tests were also made with each mixture. It was found that in nearly every case, the tinny feeling and sulphite-cellulose attributes became evident when more than 30 per cent. of sulphite-cellulose extract was used, it being noticeable more quickly in the cases of chestnut and myrobalans extract, the liquid quebracho showing the least evidences of sulphite-cellulose extract being present. The general effect was to lighten the color of the skin a little.

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THE CHEMICAL EXAMINATION OF WATERS AND TRADE EFFLUENTS.

By J. A. S. Morrison, M. Sc.

In a previous paper (this J., July 1911, pp. 326-342) the writer discussed the development of the bacterial method of sewage treatment, and its application to the treatment of tannery effluents. In the present paper it is his desire to briefly sketch methods of analysis of waters and effluents. In the main, the methods described are those regularly carried out in the laboratory of the West Riding of Yorkshire Rivers Board, a statutory authority administering rivers pollution acts in the West Riding of Yorkshire. The methods to be described have only been adopted after many experiments and comparisons with those elsewhere in use, and, recognizing the necessity for standard methods of analysis of waters and of sewage and trade effluents, the writer would urge their consideration by members of this association.

The sampling of effluents is of great importance; too little regard is generally given to this matter, and whilst analysis may be accurate for the sample under examination, the results often fail to give a correct indication of the general nature of an effluent or of its effect upon a stream. It is generally necessary to take small samples at definite intervals of time, the volume of these samples being roughly proportional to the rate of flow of the effluent. The small samples are then mixed to form one sample, which may be taken as an average of the flow during the specified time. Thus, if the rate of flow be fairly constant, samples of 200 cc. volume, taken every five minutes, will at the end of one hour, give an average sample sufficiently large in volume for all required analytical determinations. Where the rate of flow is variable, reasonable means should be taken to ensure that the sample is representative of the total discharge. If these conditions were more often observed greater uniformity of results would more often be obtained.

Before analysis, the physical characteristics of the sample should be noted. Under this heading one describes the color and turbidity of the liquid, the apparent amount and nature of

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the sediment, the odor, and the reaction to litmus paper. These are of general importance and should be noted as soon as possible, for they often change as the sample ages. The reaction to litmus paper deserves note in that its description may vary with the observer. Using the bibulous paper supplied by the Helfenberg Chemical Works Co. Ltd., Dresden, Germany, it has been found that solutions of sulphuric acid containing 1 and 2 parts per 100,000 only slowly reddened blue litmus paper; they would be classed as slightly acid. Solutions containing from 5 to 10 parts per 100,000 react almost immediately and would be classed as acid. Similarly, with solutions of caustic soda, less than 2 parts per 100,000 do not react with red litmus paper, 2 to 5 parts react but slowly and would be called slightly alkaline, whilst more than 5 parts give distinct reaction.

The chemical analysis is generally carried out on the shaken sample as discharged to stream. Occasionally analyses are performed on the liquid after filtration, but these do not give as true an indication of the extent of the pollution as do those from the analysis of the whole sample. They are nevertheless often useful in showing the influence of matters in suspension. One often finds present hairs and lumps of solid matter which cannot be broken up by shaking, and which prevent the taking of an average portion. In such cases it is advisable to run the sample through a sieve of brass wire gauze of about 1600 apertures to the square inch. The separated matters are weighed and examined, and the analysis is carried out on the liquid which has passed the sieve.

The results of analysis should, in common with British and Continental practice, be expressed in parts per 100,000. They are not really parts per 100,000 by weight, but centigrammes per liter. The error is seldom appreciable.

The methods described are in general use in the examination of sewages, waters, and trade effluents, but, seldom is it necessary to apply all of them in the analysis of a single sample. Thus, a sewage may be judged upon the physical characteristics and the chloride, oxygen absorbed, and nitric nitrogen figures. For a trade effluent, in addition to physical characteristics, the solids in suspension and solution, the oxygen ab-

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sorbed, the alkalinity or acidity, the hardness and any factor special to the sample are generally determined. The determinations carried out in the examination of a water depend upon the nature of the sample and the purposes for which it is to be used. Thus a water for boiler use or for leaching will not require the same detailed examination as one to be used for domestic purposes.

Total Solids.

This figure is the sum of the solids in suspension and the solids in solution. It is seldom directly determined.

Solids in Suspension.

The sample is shaken and a definite volume (50 to 1,000 cc. according to the amount of sediment) is withdrawn. This is then filtered through a fluted filter-paper, previously dried to constant weight. Munktell's No. 1. F. 11 cm. diameter is a very good one for this purpose. The few cubic centimeters first filtering through are carefully returned to the paper, and passed through a second time in order to ensure perfect filtration. After filtration, the paper and the solids are washed with cold distilled water, then transferred to the steam oven, and dried until constant in weight. The increase in weight gives the amount of suspended matter in the volume of sample taken. In other laboratories this figure is often obtained by determining the total solids and the solids in solution and taking the difference. The writer would urge that direct determination gives greater accuracy, as the solids in suspension in many waters and effluents are small, and therefore any errors in determination of the total and solution solids are thrown upon the figure for suspended solids. This resulting error may, in many cases, give a totally inaccurate figure for the suspended solids. Only when the sample is so thick and turbid that filtration is slow and difficult, does one determine this figure by difference. In this case, the amount of suspended solids is generally so large that errors of determination have but little effect upon the figure.

The ash of the suspended solids is determined by placing the dried paper and solids in a platinum capsule, and incinerating in a muffle furnace. The ash of the paper must be allowed for.

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Solids in Solution.

These are determined by taking a definite volume of the filtrate from the above determination, and evaporating in a weighed platinum dish, first to small bulk over a rose burner, and finally to dryness on the water-bath. The residue is then dried to constant weight in the steam oven. The ash is determined by incinerating in a muffle furnace.

Oxygen Absorbed.

This test, which is one of the most important determinations carried out in the examination of waters and effluents, gives information which is universally regarded as valuable. It is based upon the fact that organic matter absorbs oxygen from acid solutions of potassium permanganate. The extent of this absorption, whilst not giving information as to the nature of the putrescible substances present, shows to a fairly accurate degree, the purity of the effluent, when judged from the point of view of putrescibility. The following solutions are required:

Potassium permanganate N/80; this is prepared by diluting accurately standardized N/10 solution.

Sodium thiosulphate, approximately N/80; this is prepared by diluting N/8 solution, as required for each day's titrations.

Sulphuric Acid, dilute solution (1 in 4), tinged to a faint pink with potassium permanganate, in order to destroy organic matter present.

Potassium iodide, 10 per cent. solution.

The estimation is carried out as follows:—Into a 12 oz. well stoppered bottle are placed 150 cc. of distilled water and 10 cc. of the sulphuric acid solution. A suitable quantity of the effluent (10 to 50 cc.) is then added, followed by successive 10 cc. portions of the N/80 permanganate solution, until excess be present. During the whole estimation, the excess of permanganate retaining its color should never be less than 5 cc. The bottle is placed in a water-bath, and is kept at a temperature of 80° F. for four hours, being occasionally shaken, and more permanganate solution is added as required. At the end of this time, 1 cc. of the potassium iodide solution is added, and the liberated iodine is titrated with the solution of sodium

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thiosulphate, starch solution being used as indicator. This titration gives the amount of thiosulphate solution corresponding to the unused excess of permanganate. It is necessary to carry out blank tests in order to determine the exact strength of the thiosulphate solution used, and to determine the absorption of permanganate by the distilled water and reagents used. Two bottles are prepared with 150 cc. of distilled water and 10 cc. of acid. Into one is placed 10 cc., and into the other 20 cc. of the permanganate solution. They are treated similarly to the bottles containing effluent. It will be seen that the difference between the titrations of the 10 cc. and 20 cc. blanks will give the amount of thiosulphate solution which is equivalent to 10 cc. of N/80 permanganate solution, and the difference between this figure and the titration for the 10 cc. blank will give the amount of permanganate solution absorbed by the water and the acid. By subtracting the amount of N/80 permanganate absorbed by the water and acid from the amount originally added in the test, and by a further subtraction of the amount remaining after 4 hours, the amount absorbed by the volume of effluent is obtained. Since N/80 permanganate, in acid solution, is capable of yielding 0.0001 gram of oxygen per cc., the number of cc. of N/80 permanganate decolorized by 10 cc. of effluent gives the oxygen absorbed by the effluent, in parts per 100,000.

Many suggestions for the variation of this test have been offered, the most important being the alteration of the period of time during which the action of the permanganate is allowed to proceed. These variations give but little additional information, except where substances which are immediately oxidized by permanganate are present, and in this case the three minutes test is useful.

In many effluents inorganic compounds, which have not been decomposed by bacterial treatment, may be present. They may have the power of rapidly reducing permanganate in solution, and thus give an undue significance to the result. Their presence and effect should be noted by means of other determinations, and due allowance made in the interpretation of results. As is only to be expected, variations of the amount of added

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distilled water affect the result, it being found that if dilution with 150 cc. of water be omitted, higher results are obtained. It is thus necessary to emphasize the fact that, as comparable results are desired, the analysis must always be carried out in the same way, and that different workers must use one standard method.

Alkalinity or Acidity.

These determinations are carried out by titrating with N/10 solutions of hydrochloric acid or sodium hydrate. The choice of indicators is important. In alkalinity determinations one generally first titrates to phenolphthalein, adds methyl orange, and continues the titration until all the alkali is neutralized. If the alkali be present chiefly as carbonate, the results are expressed in terms of sodium carbonate, calcium carbonate, or ammonia, which ever is likely to be present. If the alkali be present chiefly as hydroxide, the phenolphthalein figure is taken, and results expressed iu terms of caustic soda or lime. In acidity determinations methyl orange is generally used, except where the acidity is due to organic acids, phenolphthalein then being used. Many effluents, containing dyes, are too deep in color to allow of the use of internal indicators. Litmus paper may then be used, or recourse may be had to the method known as spotting on a tile. In this process several separated drops of the indicator are placed on a tile and, after each addition of acid or alkali, a drop of the liquid is removed on a glass rod, and mixed with a drop on the tile until the desired tint is obtained. It sometimes happens that the dye itself will act as an indicator.

Hardness.

The hardness of waters and effluents is mainly due to the presence of salts of calcium and magnesium. From the point of view of the manufacturer the chief effect of these salts is the trouble often caused by the formation of scale when hard waters are used for steam raising. Another very important consideration is the precipitation of soap and dyestuffs from liquors in which they are dissolved.

English degrees of hardness represent grains of calcium car-

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bonate, or its equivalent, per gallon, whilst French degrees are expressed as parts of calcium carbonate in 100,000 parts of water, and German degrees as parts of calcium oxide in 100,000 parts. A water of less than 5 English degrees of hardness is considered soft, whilst if the hardness exceeds 15 degrees the water is hard.

The only accurate method of determining the hardness of a water is by a gravimetric estimation of calcium and magnesium, but two other methods may be satisfactorily employed,—Wartha's modification of Hehner's alkalimetric method, and Clark's soap, test. The former of these two methods is certainly more scientific, but Clark's method is sufficient for many technical, and most hygienic analyses.

From the point of view of a Rivers Authority, the hardness of an effluent must be judged on the basis of its boiler scale forming and soap destroying powers. It must be remembered that many textile manufacturers must use river water for washing purposes, whilst the majority depend upon it for steam raising. When these points are considered it will be seen that an expression of the soap destroying power is valuable. This, in the opinion of the writer, is best obtained by the use of Clark's soap test method which is speedy in application and gives reasonably accurate results. Hehner's method on the other hand, is particularly applicable to the analysis of waters as distinguished from trade effluents, and the writer would suggest its use on those occasions when accurate examinations of water supplies are being carried out. The methods are outlined below.

Clark's method.

Two solutions are required. A standard soap solution and a standard hard water. The preparation and standardization of these solutions is so generally detailed in various text books that repetition is not necessary. The method of titration is important in that different operators may differ in their interpretation of the end point. If, however, each operator always titrates to the same end point that he has used in standardizing his soap solution, different observers will get concordant results.

Total Hardness.

Fifty cc. of the sample are placed in a well stoppered 10 oz.

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bottle and the soap solution added, one cc. at a time. The mixture is well shaken after each addition, and titration continued until a lather is formed which lasts and covers the whole surface for five minutes. A good indication of the end point is also given by the sound emitted by the shaken liquid. As the titration is completed the hard metallic sound quickly changes to a soft one. In addition, the change in the feel of the bottle, when shaken, indicates that sufficient soap solution has been added. If 50 cc. of the sample require more than 16 cc. of the soap solution the sample is diluted to a suitable strength and 50 cc. of the diluted liquid taken. From published tables showing the amounts of $CaCO_3$ per 100,000 corresponding to definite volumes of standard soap solution the total hardness may be calculated.

Permanent Hardness.

A definite volume of sample is boiled to a small bulk, diluted to 50 cc. volume with distilled water, and filtered. The filtrate is then shaken with soap solution as above, and the permanent hardness calculated from the tables.

Temporary hardness is taken as the difference between the total hardness and the permanent hardness, and corresponds approximately to the originally dissolved bicarbonates.

Hehner's Method.

Temporary Hardness.

One-hundred cc. of the water are titrated with N/10 hydrochloric acid in a porcelain dish, using a 1 per cent. Alizarin paste as indicator, until a yellow coloration is obtained. The liquid is then heated to boiling, and the titration continued until the yellow coloration is permanent. If 100 cc. of water be used, each cc. of N/10 acid equals 5 parts $CaCO_3$ per 100,000.

Permanent Hardness. (Pfeifer and Wartha's modification of Hehner's method.)

A special alkaline reagent is required, and is made by mixing equal volumes of N/10 sodium hydrate and N/10 sodium carbonate solutions.

Fifty cc. of the reagent are mixed with 200 cc. of the water in a Jena flask. The liquid is then boiled to a volume less than 200 cc., cooled, made to 200 cc. volume with distilled water, and the

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precipitate allowed to settle. One-hundred cc. of the clear liquid, corresponding to 100 cc. of the water and 25 cc. of the N/10 reagent, are pipetted off and titrated with N/10 hydrochloric acid, using methyl orange as indicator. The difference between this titration and 25 cc. N/10 alkali represents the alkali used to precipitate calcium and magnesium salts causing permanent hardness. Each cc. difference represents 5 parts $CaCO_3$ per 100,000.

Pfeifer and Wartha's modification is important in that it embraces the use of sodium hydrate in addition to sodium carbonate. Sodium carbonate alone will not completely precipitate magnesium salts. A good excess of sodium hydrate and carbonate is necessary in order to lessen the solubility of calcium carbonate and magnesium hydroxide. The calcium and magnesium salts causing temporary hardness will also be precipitated by the reagent, but, as sodium bicarbonate in equivalent quantity will be formed, the alkalinity will not be affected by this temporary hardness.

ESTIMATION OF MAGNESIUM SALTS CAUSING PERMANENT HARDNESS.

Winkler's Method.

This method depends upon the fact that calcium hydrate does not precipitate lime salts, but precipitates magnesium salts as hydrate. If iron be present it will also be precipitated by lime. It must thus be separately estimated colorimetrically and allowed for: 0.3733 gram ferric iron equal 0.24 gram magnesium.

The estimation is as follows:—One-hundred cc. of the water are neutralized with N/10 hydrochloric acid, using alizarin as indicator, as in the determination of temporary hardness. It must be noted that if this neutralization were not carried out, the subsequent addition of lime-water would cause precipitation of bicarbonates and thus vitiate the result. A definite volume of clear lime-water (25 or 50 cc.)—at least 50 per cent. in excess of that required for precipitation of the magnesium salts—is then placed in a 200 cc. graduated flask. The hot neutralized water is rinsed in from the dish, and the flask filled just to the mark with distilled water. The flask is then stoppered, the contents shaken, and warmed on the water-bath for 30 minutes. The flask is then

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cooled, and, after making to 200 cc. volume, the precipitate is allowed to settle. One-hundred cc. of the clear liquor are then pipetted off, and titrated with N/10 hydrochloric acid, phenolphthalein being used as indicator. If this titration be multiplied by two, and the product be subtracted from the number of cc. of N/10 lime-water used, the result will express the number of cc. of N/10 lime-water required to precipitate magnesium salts in 100 cc. of the water under examination.

Each cc. thus required $\times$ 5.0 = Mg salts expressed in terms of $CaCO_3$
Each cc. thus required $\times$ 1.2 = Mg salts expressed in terms of Mg
Each cc. thus required $\times$ 2.0 = Mg salts expressed in terms of MgO

In summary, it may be said that each method has its value for specific purposes, and that judgment in the selection of one or the other method is necessary.

We have now discussed those determinations which are generally carried out in routine examinations, and from the results obtained one can generally judge the purity of an effluent. Many other determinations, however, give valuable results, and may be briefly considered.

Chlorides.

These are generally expressed in terms of sodium chloride. They are determined by titration of portions of the filtrate (50 to 100 cc.) with standard silver nitrate solution, using potassium chromate as indicator. As the method is only accurate in neutral or slightly alkaline solutions, the filtrate must be made nearly neutral. Acid solutions are best neutralized with calcium carbonate, the excess being filtered off before titration, whilst alkaline solutions should be neutralized with nitric acid. If sulphides be present in the sample, or if the color render titration difficult, it is necessary to take to dryness with a few cc. of lime-water, and to gently char the residue. The mass is then treated with warm water, and chlorides are estimated in the solution after filtering.

Silver nitrate solution of strength N/11.7 should be used for titration. Each cc. of this solution equals 0.005 gram sodium chloride.

Nitrogen.

The nitrogen content of an effluent or water is expressed ac-

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cording to the forms in which the nitrogen is present. One thus determines nitrogen under the following heads, ammoniacal, albuminoid, organic, nitric and nitrous. These will be discussed in detail.

For these determinations a good supply of ammonia-free distilled water is necessary. This is best made by adding a few cc. of 10 per cent. sodium carbonate solution to about 1 liter of distilled water, and boiling in a retort until the distillate is free from ammonia as shown by Nessler's reagent. In this way a good stock may speedily be obtained, and stored for use in water holders.

Ammoniacal Nitrogen (from free and saline ammonia).

A suitable quantity of the sample is added to about 600 cc. of ammonia-free water in a retort. The whole is made slightly alkaline by the addition of a few drops of 10 per cent. sodium carbonate solution, and the liquid is distilled into 100 cc. Nessler glasses until a distillate is obtained which is free from ammonia, as shown on the addition of 2 cc. of Nessler's reagent. The successive portions are Nesslerized and matched with standards made by Nesslerizing known volumes of a solution of ammonium chloride of standard strength. For this purpose a solution containing 0.00001 gram nitrogen per cc. is necessary, and is best made by dissolving 3.8214 grams of pure ammonium chloride in a liter of ammonia-free water, and then diluting this strong solution 100 times when required. This dilute solution then contains ammonium chloride equivalent to 0.00001 gram nitrogen per cc.

In many clear waters the estimation may be made by Nesslerizing without distillation. The presence of salts in solution however, renders it advisable to always distil from a retort. Very often the distillate is quite turbid, especially is this so if the sample contains fats, and it is then necessary, before Nesslerizing, to filter through a paper which has been washed with ammonia-free water. The solid distillate remaining on the paper does not contain nitrogen as free and saline ammonia.

Albuminoid Nitrogen.

Wanklyn in 1867, (J. C. S., 1867 Vol. 20, p. 445) devised this test for the examination of sewages and effluents. It depends upon

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the fact that complex nitrogenous organic bodies are partially decomposed when distilled with an alkaline solution of potassium permanganate, with liberation of ammonia. This gives an indication of the amount of organic matter which is liable to undergo putrefactive decomposition. It must be understood that the test is, like the oxygen absorbed test, only a comparative one, and has a similar value. It is, however, more tedious to perform, and often does not furnish any additional information. In fact, there is an almost constant relationship existing between the results obtained by the two processes, varying only, with the nature of the liquid.

The method of determination is as follows.

To the liquid remaining in the retort after estimation of free and saline ammonia are added 25 cc. (or more in the case of very bad samples) of a solution containing 8 grams of potassium permanganate and 150 grams of sodium hydroxide per liter. The distillation is then commenced, and ammonia is estimated in the successive portions of the distillate by Nesslerization. Experience will show that, with the majority of effluents, the point at which ammonia ceases to come over is scarcely ever reached. It would seem that concentration of the liquid in the retort brings about decomposition of the more stable nitrogenous organic bodies, and that one gradually gets action similar to that occurring in the Kjeldahl process. The point at which distillation must be stopped is thus dependent upon the judgment of the operator. One generally finds that the amounts of ammonia in successive portions are in a fairly constant ratio, and that when the later portions give excessive amounts in comparison with previous portions, the secondary decomposition has set in; the distillation should then be stopped.

Organic Nitrogen.

The organic nitrogen figure is represented by the difference between the total nitrogen and the nitrogen due to free and saline ammonia. The total nitrogen is obtained by the Kjeldahl process, as follows.

A suitable amount of the sample (25 cc. will be sufficient in the case of an average effluent) is heated with 10 cc. of redistilled concentrated sulphuric acid in a 300 cc. Jena flask. In

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the majority of cases there is no necessity for addition of potassium sulphate during the digestion, charring steadily takes place, and heating may be stopped usually in about two or three hours time after the liquid has become colorless. The liquid, after cooling and diluting, is neutralized with a concentrated ammonia-free solution of caustic soda. It is then transferred to a 700 cc. Jena flask and diluted with ammonia-free water to about 400 cc. volume. Distillation is then carried out, and the ammonia in the distillate is estimated by Nesslerizing. Where a large amount of ammonia is likely to be present it is more convenient, and quite accurate, to distil into a measured excess of N/10 acid, and to titrate the excess acid remaining with N/10 alkali. The nitrogen content is calculated from the amount of standard acid used up by the distillate. The amount of nitrogen estimated by the Kjeldahl process, less that from free and saline ammonia, is termed organic nitrogen.

Examination of analytical data of several hundred samples of different effluents by the chief chemist of the West Riding Rivers Board has shown that, for liquids of a similar nature, the ratio of the organic nitrogen to the albuminoid nitrogen is fairly constant. Thus, for good river waters the ratio is about 6.0; for more polluted waters the ratio drops to about 3.0, whilst crude sewages give 3.0, and sewage effluents 4.0 to 3.0. In grossly polluting trade effluents the ratio sinks to 2.0 or even lower.

Nitrous Nitrogen.

Two methods are in general use for this determination, the choice depending upon the amount present. The sulphanilic method is used when small amounts are present, generally below 0.005 parts per 100,000. The metaphenylenediamine method is used when the quantity exceeds this figure, the sulphanilic acid method then being too sensitive, and giving colorations which are too deep to accurately match.

Sulphanilic Acid Method.

The reagent consists of two solutions.

(1.) Eight grams pure sulphanilic acid dissolved in 1,000 cc. 5N acetic acid.

(2.) Five grams α-naphthylamine dissolved in 1,000 5N acetic

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acid. If turbid, the solution should be filtered through washed absorbent cotton.

To a definite volume of the sample are added 2 cc. of each of the solutions. A series of standards is at the same time made up by using a standard solution of sodium nitrite. After standing 5 to 10 minutes the coloration produced in the sample is matched with the standard colors produced under the same conditions. The standard sodium nitrite solution is made as follows.

1.1 gram silver nitrite is dissolved in nitrite free water, sodium chloride solution is added, the precipitated silver chloride is filtered off, and the filtrate and washings made to 1,000 cc. volume. This solution contains 0.0001 gram nitrous nitrogen per cc., but is too concentrated for use in estimations. It should be diluted 100 times when required. One cc. then equals 0.000001 gram nitrous nitrogen. This dilute solution should be kept in a sterilized bottle, and 1 cc. of chloroform added as a preservative.

Metaphenylenediamine method.

Two solutions are necessary.

(1.) Eight grams metaphenylene diamine hydrochloride dissolved in 1,000 cc. water.

(2.) Sulphuric acid 1 in 4.

To a suitable quantity of the effluent (10 to 50 cc.) in a Nessler glass is added 1 cc. of each solution. The brown color produced, if nitrites be present, is then matched with that produced by known amounts of standard sodium nitrite solution.

It may be said that the determination of nitrous nitrogen is seldom necessary and then only when samples of drinking and river waters are under detailed examination. Nitrites in an effluent absorb oxygen from solutions of potassium permanganate, thus increasing the oxygen absorbed figure. Experience has shown that errors in the latter figure due to nitrites are so small that corrections have very little effect, and seldom, if ever, affect the classification of the effluent as good or bad.

Nitric Nitrogen.

This estimation is a most important one, and should be carried out as soon as possible after the sample has been taken.

All methods of purification aim at the conversion of the nitro-

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gen of the organic matter into nitrates by oxidation. The presence of nitrates then gives an indication of purification. Another quite important fact is that effluents containing organic matter as well as nitrates undergo changes on standing. The nitrates then act as oxidizing agents, and continue the purification to a further stage. For this reason, an effluent containing nitrates is more favorably classified than one having the same oxygen absorbed figure but being free from nitrates.

Many methods of estimation have, from time to time, been proposed, but no method has been noted to have the same advantage as the phenol sulphonic acid method. (Grandaval and Lajouse, Comptes Rendus, July 6, 1885.) For this method, a solution of phenol sulphonic acid is made as follows:—Eighteen grams of phenol and 9 cc. of distilled water are mixed in a beaker, 111 cc. of concentrated sulphuric acid are then carefully added, and the solution is digested on the water-bath for six to eight hours, after which it is ready for use. Omission to digest on the water-bath generally results in the production of a green color during estimations instead of the yellow required.

The estimation is then carried out as follows:

Twenty-five cc. of the filtered effluent are evaporated to dryness in a porcelain basin on the water-bath. One cc. of the phenol sulphonic acid and 1 cc. of water are added to the residue, and heating on the water-bath is continued for two to three minutes. A slight excess of ammonia or potash is then added. If nitrates are present a yellow coloration is produced. At the same time 10 cc. of a standard solution of potassium nitrate (1 cc. = 0.00001 gr. nitrogen) are evaporated to dryness, and a standard color produced by adding the phenol sulphonic acid as described. The color produced by the effluent is then matched with known portions of the standard color, and the nitrates thus estimated.

Attempts to determine the nature of the coloring matter produced have not been successful. It has been supposed that picric acid is this coloring matter, but various observers have been unable to match the color with solutions of this compound. It is probable that the color consists of mono, di, and tri nitrophenols in certain complicated proportions. This method has one weak point in that it yields low results in the presence of

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chlorides. Tatlock and Thomson (J. S. C. I. 1904, p. 428) found that the presence of chlorides, in amounts generally found occurring in sewages, gave results 10 to 20 per cent. below the truth. This difficulty is easily overcome by precipitating almost all the chlorides with a standard solution of silver sulphate free from nitrates, filtering off, and estimating nitrates in the filtrate and washings. The writer has, at times, successfully worked the Brucine test for the estimation of nitrates in waters. One cc. of the water under examination is added, drop by drop, to 3 cc. of pure sulphuric acid in a Nessler glass, and the whole cooled. A few milligrams of brucine are then added from a spatula. A pink color develops if nitrates are present. By judicious use of a dilute solution of potassium nitrate (1 cc. = 0.00002 gram nitrogen) a series of standards can at the same time be made, and fairly accurate results obtained. The sulphuric acid must be free from nitric acid, and the mixture be cool before addition of the brucine.

Oxygen in solution.

The oxygen in solution is measured by a process devised by Winkler and modified by Rideal (Analyst, 1901, Vol. 26, p. 141). The method is carried out as follows. A stoppered bottle of capacity about 250 cc. is carefully filled with the liquid under examination. To this are added 1 cc. of a solution of sulphuric acid (1 in 4) and a few drops of N/10 potassium permanganate in order to oxidize nitrites. If a permanent pink color be not obtained, more potassium permanganate must be added. The liquid is now decolorized by addition of one or two crystals of potassium oxalate. There are added 1 cc. of a 33 per cent. solution of manganous chloride and 1 cc. of a solution containing 33 per cent. sodium hydroxide and 10 per cent. potassium iodide. White manganous hydrate is precipitated at this stage, and absorbs any dissolved oxygen. The bottle is carefully stoppered with exclusion of air, and well shaken. After 3 minutes, 2 cc. of concentrated hydrochloric acid is added. Liberation of iodine occurs, and this is then titrated with N/80 sodium thiosulphate, starch being used as indicator. Each cc. of N/80 sodium thiosulphate equals 0.001 gram oxygen, or 0.07 cc. of dissolved oxygen measured at 0° C. and 760 mm. pressure. In sampling the liquid, and throughout the test, great care must be taken to

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exclude air bubbles. The best method of sampling is to use a small aspirator bottle of 250 cc. capacity, and to fill it in a bucketful of the sample by partly immersing in the liquid, removing the bottom stopper, and when full, restoppering. Samples containing any matter in suspension which may interfere with the reaction should be clarified by addition, to a large sample, of 3 cc. of a saturated solution of aluminium chloride followed by 3 cc. of a saturated solution of sodium carbonate. The precipitated aluminium hydroxide brings down the suspended matter. The clear liquor may be siphoned into a 250 cc. bottle, and the dissolved oxygen then estimated. It must be understood that the dissolved oxygen in a sample gradually diminishes in amount as the sample ages. It is thus often necessary to take river samples, and to immediately proceed with the estimation as far as the precipitation of the manganous hydrate. The sample will then keep quite well until the rest of the estimation can be finished in the laboratory.

In his previous paper the writer has written on the importance of oxygen in solution as an aid to the regeneration of streams. It is thus of importance to be able to judge the effect of the addition of an effluent to a stream. Samples of the effluent are mixed with different volumes of fully aerated tap water, the oxygen in solution is quickly determined in one portion, and the rate of absorption of the dissolved oxygen by the effluent is determined by estimation of the amount present in the mixtures after certain periods of time.

The putrescibility test devised by Scudder is carried out in this way, and is of considerable value.

Another test, frequently carried out, is to aerate the sample by shaking it with air in a stoppered bottle, dividing into two parts, and estimating the dissolved oxygen, immediately in one half, and in the other after keeping for 24 hours. The effluent is judged to be unsatisfactory if the amount of dissolved oxygen remaining falls below 50 per cent. of that in the first half.

Putrescibility.

Many tests for putrescibility have, from time to time, been suggested. Mention has already been made of the one devised by Scudder.

The one in general use in the laboratory of the Rivers Board

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is carried out by incubating the effluent at 80° F., in stoppered bottles from which air is excluded. The bottles are carefully observed from day to day, and the time noted when putrefaction occurs. The signs of putrefaction are blackening of the effluent, formation of sediment, evolution of sulphuretted hydrogen, and increase in the oxygen absorbed in three minutes. It must, however, be suggested that this and similar tests are not as valuable as the determination of the oxygen dissolved.

Fatty matter.

It is very often necessary to determine fatty matters present in an effluent. This estimation is carried out by acidifying a portion of the sample (50 to 200 cc.), allowing to stand for sometime in order to separate fatty matters, and then filtering through paper. The paper, after washing with cold distilled water, is dried in the steam oven, cooled, weighed, placed in an extraction thimble, and extracted with ether in a Soxhlet apparatus. After extraction, the ether is distilled off, and the increase in the weight of the flask determined. At the same time the loss in weight of the paper is noted, and serves as a check on the other weighing.

Sulphur Compounds.

Many effluents are liable to contain sulphur compounds in the form of free sulphur, thiosulphates, sulphites, sulphates, and sulphides. It is difficult to estimate these separately. What is generally done is to estimate the sulphur present as sulphate in one portion of the sample, and the total sulphur in another portion. The sulphur in forms other than sulphate is thus estimated by difference.

The sulphates are estimated by precipitating, in hydrochloric acid solution, as barium sulphate. From the weight of the precipitate the amount of sulphur present in this form can be easily calculated.

Total sulphur is estimated by oxidation to sulphate in alkaline solution, and precipitating as barium sulphate. A portion of the sample is rendered alkaline by addition of 10 cc. of a 10 per cent. solution of sodium hydrate, a few crystals of potassium permanganate are then added and the whole boiled for some minutes. After partial cooling, a few drops of concentrated

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hydrochloric acid are added, and the liquid boiled until colorless and clear. Filtration, if necessary, is carried out, and sulphates are then precipitated with barium chloride.

A blank estimation is generally carried out on the sodium hydrate solution, and is allowed for. The estimation is best made in an Erlenmeyer flask with a funnel in the neck to prevent loss by spurting.

The writer finds this method of use in the estimation of sulphides in lime liquors.

It may be noted that the evolution of sulphuretted hydrogen in the putrescibility test is due to the presence of albuminoid bodies containing sulphur. It will thus be seen that, for any particular liquor which may contain these complex bodies, the sulphur content may furnish information which will give an indication of its liability to putresce. In sewage, for example, determinations in a few cases have shown the presence of sulphur in forms other than sulphate varying between 1.7 and 3.5 parts per 100,000.

Iron.

Iron in a water or effluent is estimated by well known colorimetric methods.

Total Iron.

A portion of the sample is evaporated to dryness with 5 cc. concentrated hydrochloric acid and 1 cc. concentrated nitric acid, redissolved in water and transferred to a Nessler glass. One cc. of concentrated hydrochloric acid and 5 cc. of a 10 per cent. potassium sulphocyanide solution are added. The red coloration produced is matched with that produced by using a standard solution of a ferric salt (1 cc. = 0.00001 gram iron).

Ferrous Iron.

To 50 cc. of the sample are added 2 cc. concentrated sulphuric acid and 15 cc. freshly prepared 0.5 per cent. solution of potassium ferricyanide. The color produced is quickly matched with a series of standards similarly made with standard ferrous ammonium sulphate solution (1 cc. = 0.0001 gram iron).

Ferric Iron is taken as the difference between the total and the ferrous iron.

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Interpretation of results.

The writer, in his previous paper, has pointed out the factors in an effluent which lead to pollution and it should be the aim of those in charge of works to minimize the effect produced by the presence of such bodies. To this end, the organic matter in suspension and in solution should be as low as possible. The effect of matters in suspension is shown by the difference in the figures for the oxygen absorbed given by the filtered and unfiltered sample. The oxygen absorbed figure should be as low as possible, but in this connection the possibility of further purification by nitrates in solution should not be forgotten. In a good effluent the latter should always be present. Alkalinity or acidity should be effectively controlled. Pollution in this direction shows inefficient precipitation or neutralization, and consequently poor control of the plant. Chlorides may be due to many causes. In waters, especially if nitrates be present, they point to sewage contamination. In sewage effluents chlorides are naturally present, and for any particular effluent, give an indication of the strength of the original sewage. In a works effluent they are not very significant, as they may be derived from products in use in various processes. The putrescibility tests, as has been explained, are not so important as those for oxygen absorbed and oxygen dissolved. Efficient aeration in the bacterial beds will help to increase the latter figure and thus lessen the possibility of putrefaction. The figures for ammoniacal, albuminoid and organic nitrogen will give an indication of the purification effected. A low albuminoid nitrogen figure should be attained, and this, coupled with a fairly high ratio between the organic and albuminoid nitrogen figures, shows good results. Other determinations such as fatty matter, sulphur compounds, and iron have a significance peculiar to the particular effluent, and their presence cannot but be harmful to a stream.

Standards of Purity.

Whilst it is impossible to define fixed standards with which an effluent must comply in order to be regarded as satisfactory when discharged to a stream, it is yet necessary to have a working standard. Sewage effluents may be judged upon the oxygen absorbed in 4 hours at 80° F. The presence or absence of nitric nitrogen must, however, be considered in addition. When

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the oxygen absorbed in 4 hours at 80° F. is less than 1 part per 100,000 the effluent is considered satisfactory, even if no nitrates are present. When nitric nitrogen is present to the extent of 0.1 part per 100,000 the effluent is considered satisfactory until the oxygen absorbed exceeds 2 parts per 100,000. Samples complying with this standard are generally found to be non-putrescible, and do not lose more than 50 per cent. of the oxygen in solution after being fully aerated and kept for 24 hours. The Royal Commission on Sewage Disposal in its Fifth Report has made a provisional recommendation as to standards for sewage effluents. The commissioners say that an effluent would usually be satisfactory if it:—

(1.) Contained not more than 3 parts per 100,000 of solids in suspension.

(2.) After filtration through paper, absorbed oxygen from the air or from a large excess of aerated water to the extent of

(a) Not more than 0.5 parts per 100,000 in 1 day.

(b) Not more than 1.0 parts per 100,000 in 2 days.

(c) Not more than 1.5 parts per 100,000 in 5 days.

This recommendation has not, however, found universal acceptance amongst chemists, and a further pronouncement by the commission is awaited with interest.

Trades effluents must be judged on somewhat similar lines, but at the same time other factors must be considered. Solids in suspension must be kept low, and should never exceed 10 parts per 100,000. The oxygen absorbed in 4 hours at 80° F. should be below 2.0 parts per 100,000. A sample having an acidity or an alkalinity, respectively due to mineral acids or to alkalies such as sodium carbonate or lime, to the extent of 10 parts per 100,000 should be considered harmful. The figures for other determinations must, in the main, be considered as confirming pollution denoted by high values for the oxygen absorbed and for suspended solids.

Waters for special purposes must be judged in the light of requirements. No standards can here be suggested.

In conclusion, the writer wishes to express his thanks to Dr. H. Maclean Wilson and Dr. H. T. Calvert of the West Riding of

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Yorkshire Rivers Board for permission to reproduce the above methods, all of which have been investigated and proved successful in the Board's laboratory.

LEEDS, ENGLAND.

REPORT ON LEATHER ANALYSIS.

By F. P. Veitch.

The committee is indebted to Mr. J. S. Rogers for the detail work in connection with the preparation and sending out of samples, the tabulation of results and the segregation of the comments of analysts.

The questions studied this year are:

1st. The time required for extracting fats.

2d. A comparison of several methods of extracting water soluble materials.

3d. A comparison of basic and normal lead acetate as clearing agents in the sugar determination.

Two samples of leather were used: No. 1, an oak tanned sole leather containing originally 0.6 per cent. of sugar, calculated as dextrose, to which was added 7.73 per cent., making a total of 8.33 per cent. of sugar, calculated as dextrose, in the prepared sample; No. 2 was an oak tanned heavily greased harness leather. After preparation, both samples were quickly and thoroughly air dried and placed in air-tight Mason jars.

The following directions were sent out.

DIRECTIONS FOR LEATHER WORK. A. L. C. A. 1911.

Fat Extraction.

Place 15 grams of the sample as received in an S and S thimble, and extract in a Soxhlet extractor, using petroleum ether, distilling between 50 and 80 degrees C, as directed under A', B, C, and D. Heat at such a rate that the liquid siphons approximately 4 times an hour.

(A) Extract two portions, 15 grams each, for 24 hours; save the leather residue; evaporate the ether from the extract on a steam bath, and dry to constant weight in a water oven, weigh and calculate the per cent. fat present (A should be

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completed, and the amount of fat determined before B, C, and D are started).

(B) Extract two portions of 15 grams each for six hours.

(C) Extract two portions of 15 grams each for eight hours.

(D) Extract two portions of 15 grams each for ten hours.

Save the leather residues from B, C and D, determine the fats in each extract as in A, and if the fat has not all been extracted in the stated time, continue until the extraction is complete, noting in each case the time required and the color, consistency, and odor and general appearance of the fat residue.

Reserve the leather residue from the fat extraction for the extraction of the uncombined tannins and non-tannins, bringing them to an air-dry condition before this extraction is begun.

1. Place the two residues of A together with the two residues of B together. Use these as duplicates for the extraction by the A. L. C. A. method (E).

2. Take the two residues from C and use these as duplicates for the extraction by the method of the Bureau of Chemistry (F).

3. Take the two residues from D and use as duplicates for the extraction by the alcohol method (G).

EXTRACTION OF UNCOMBINED TANNINS AND NON-TANNINS.

(E) Method of A. L. C. A.

Digest the leather residues A and B as duplicates in percolators over night, transfer the extract to a 2 liter flask, then extract with water at 60° C for three hours, removing the extract from a side tube of the extractor, thus avoiding boiling the extract. The total volume of solution to be 2 liters; determine the glucose, soluble solids and non-tannins as directed below:—

(F) Method of the Bureau of Chemistry.

Take the leather residues from C and moisten thoroughly with distilled water. Transfer leather and water to a Soxhlet, extractor, and place cotton above and below the leather in the extractor, to prevent it from being carried over at the time of syphoning. The cylinder of the extractor shall be surrounded by a water-bath, kept at 50° C. At the beginning of the extraction, pour 250 cc. of distilled water (including that used in

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moistening the leather) into the Soxhlet and allow it to syphon into the flask below, then begin the boiling. At the end of the first hour, remove the flame and transfer the extract to a one liter graduated flask, add 200 cc. distilled water to the Soxhlet and continue the extraction for two hours. Remove the extract, add 200 cc. of water and continue the extraction for five hours and remove the extract. Make one more extraction, adding 200 cc. of water as before, and continuing the extraction for six hours. This gives fourteen hours extraction, and an extract that does not exceed one liter in volume. Make the extract up to one liter at room temperature and use as directed below, for the determination of glucose, soluble solids and non-tannins.

(G) Alcohol method.

Take the two leather residues from D (they may be extracted in the same thimble in which the ether extraction was made after they come to an air-dry condition) and extract with 95 per cent. alcohol for eight hours in a Soxhlet extractor. Add 250 cc. of water to the extract and evaporate the alcohol on the steam bath, make the solution to one liter, at room temperature and determine glucose, soluble solids and non-tannins as directed below. (It has been shown that alcohol extracts much glucose and some epsom salts.)

GLUCOSE.

(a) To 200 cc. of the extract add 25 cc. of a saturated solution of normal lead acetate, mix thoroughly, allow to stand about 15 minutes, and filter. The funnels and beakers must be kept covered to prevent evaporation. Remove the lead from the filtrate by adding a slight excess of solid potassium oxalate and filtering. Pipette 150 cc. of the last filtrate into a 600 cc. Erlenmeyer flask and add 5 cc. of concentrated HCl and boil under a reflux condenser for two hours, cool, neutralize with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (This filtrate must be clear.) Use 50 cc. of this filtrate for the determination of sugar. Determine as directed in the methods J. A. L. C. A., Vol. VI, No. 1, p. 12.

(b) Determine sugar in the same manner as in (a) ex-

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TABLE I.—THE EXTRACTION OF FAT BY PETROLEUM ETHER.

		Sample No. 1				Sample No. 2, ether extract			
		6 hours	8 hours	10 hours	24 hours	6 hours	8 hours	10 hours	24 hours
J. R. Blockey[1]	Leathersellers Co's Technical College, London	2.07	2.10	2.05	2.16	28.80	29.00	29.30	29.40
		2.00	2.10	2.10	2.07	29.00	29.20	29.40	29.60
M. F. Nichols	Nichols' Laboratory, Grand Rapids, Mich.	2.04	2.09	2.08	2.09	29.33	29.10	29.72	29.74
		2.06	2.05	2.04	2.08	30.00[3]	29.30	30.00[3]	29.47
J. M. Seltzer.....	Kistler, Lesh & Co., Lock Haven, Pa.	1.97	2.02	2.00	2.09	29.17	29.11	29.47	29.54
		1.95	2.00	1.98	2.07	29.13	29.13	29.35	29.40
J. S. Rogers	Bureau of Chemistry, Washington, D. C.	1.98	2.02	2.02	2.05	29.27	29.47	29.63	29.64
		1.97	1.98	2 04	2.06	29.39	——	29.63	29.67
B. J. Ray[2]	Agricultural Experiment Station, Raleigh, N. C.	2.03	1.99	2.15	2.04	29.25	25.19[3]	29.41	29.47
		1.97	——	2.10	2.06	——	——	——	29.30
P. F. Trowbridge	Agricultural Experiment Station, Columbia, Mo.	1.99	1.99	1.97	1.92	29.06	28.92	29.29	29.23
		2.17	1.90	1.99	1.99	28.78	28.39[3]	29.30	[3]28.92
T. A. Faust.....	Yocum Laboratory, Newark, N. J.	2.01	2.12	2.02	2.27[3]	28.97	28.95	29.33	29.68
		2.07	2.17	2.19	2.31[3]	29.01	29.30	29.14	29.38
Averages		2.02	2.04	2.04	2.05	29.09	29.14	29.41	29.49

[1] The siphonings occurred from 6–8 times per hour.

[2] The results 25.19[3] is thought to be too low on account of the leather being too tightly packed in the extraction thimble.

[3] All results marked with (3) are not included in the averages.

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TABLE II.—LEATHER EXTRACTION AND ANALYSIS OF THE EXTRACT. Sample No. 1.

Extracted by	A. L. C. A. method					Bureau of Chemistry method					Alcohol method				
	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]
J. M. Seltzer, Kistler Lesh & Co..	23.4	12.7	10.7	8.28	6.60	24.7	12.4	12.3	8.30	6.60	25.1	12.0	13.1	8.13	6.48
	23.0	12.7	10.3	8.42	6.72	24.0	12.2	11.8	8.46	6.68	25.6	12.6	13.0	8.20	6.52
J. S. Rogers, Bureau of Chemistry	22.7	11.3	11.4	8.07	6.50	25.2	11.0	14.2	7.92	5.09	25.0	11.4	13.6	8.02	—
	23.0	11.2	11.8	8.41	6.38	24.6	10.6	14.0	8.20	6.22	26.1	11.4	14.7	8.02	—
B. J. Ray,[3] N. C. Agri. Expt. Station	20.8	—	—	0.50*	—	22.0	—	—	6.13*	—	23.9	—	—	7.59*	—
	27.4	—	—	0.42*	—	23.6	—	—	3.96*	—	24.6	—	—	7.63*	—
J. R. Blockey,[4] Leathersellers Co's Technical College, London....	24.5	12.2	12.3	8.60	7.40	—	—	—	—	—	20.3*	10.6	9.7*	6.05	4.35
	24.1	12.6	11.5	8.70	7.60	—	—	—	—	—	20.4*	10.6	9.7*	6.00	4.20
	24.4	12.8	11.6	8.70	7.58	—	—	—	—	—	—	—	—	—	—
M. F. Nichols, Nichols' Laboratory, Grand Rapids, Mich.....	19.2	11.6	7.6*	—	—	17.3*	10.6	6.7*	—	—	22.5	12.1	10.4	—	—
	22.0	11.1	10.9	—	—	—	—	—	—	—	—	—	—	—	—
T. A. Faust, Yocum Lab., Newark, N. J.	25.4	12.1	13.3	8.70	6.65	23.7	11.8	12.9	—	—	25.7	11.5	14.2	7.45[5]	[5]5.90
	25.9	12.3	13.6	8.41	6.75	—	—	—	—	—	25.7	11.5	14.2	7.45[5]	—
	—	—	—	7.27*[5]	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	7.52*[5]	—	—	—	—	—	—	—	—	—	—	—
Average soluble solids	23.5	—	—	—	—	24.0	—	—	—	—	24.9	—	—	—	—
Average non-tannins..	—	12.0	—	—	—	—	11.4	—	—	—	—	11.9	—	—	—
Average tannins.....	—	—	11.6	—	—	—	—	13.0	—	—	—	—	13.3	—	—
Average glucose (A)..	—	—	—	8.47	—	—	—	—	8.22	—	—	—	—	7.41	—
Average glucose (B)..	—	—	—	—	6.90	—	—	—	—	6.15	—	—	—	—	5.49

[1] Glucose (A)—The sugar solutions for these determinations were cleared by normal lead acetate.

[2] Glucose (B)—The sugar solutions for these determinations were cleared by basic lead acetate.

[3] The extracts used by Mr. Ray for sugar determinations stood about two weeks before being analyzed, and considerable fermentation had taken place shown by growths on the surfaces of the solutions. This undoubtedly explains the results obtained.

[4] Mr. Blockey converted the Cu_2O in the sugar determination into CuO and weighed in that form. He fouud that the results obtained by this method checked with those obtained by the prescribed method.

* Results marked thus (*) are not included in the averages.

[5] Sodium carbonate was used in excess instead of potassium oxalate for removing the lead.

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TABLE III.—LEATHER EXTRACTION AND ANALYSIS OF THE EXTRACT.

Sample No. 2.

Extracted by	A. L. C. A. method					Bureau of chemistry method					Alcohol method				
	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]	Soluble solids	Non-tannins	Tannins	Glucose A[1]	Glucose B[2]
J. M. Seltzer, Kistler Lesh & Co...	14.1	5.6	8.5	2.68	1.92	14.3	5.7	8.6	2 65	1.88	12.7	5.0	7.7	2.25	1.55
	13.9	5.7	8.2	2.64	1.83	14 7	6.0	8 7	2.67	1.90	12.3	4.9	7.4	—	—
J. S. Rogers, Bureau of Chemistry	13.0	4.9	8.1	2.50	1 41	17.6	5 3	12.3	2.23	1.34	13.8	4.1	9.7	2.24	—
	13.7	4.9	8.8	2.21	1.30	17.8	5.1	12.7	2.13	1.46	13.5	4 2	9.3	2.07	—
B. J. Ray,[3] N. C. Agri. Expt. Station.....	16.6	—	—	0.00*	—	15.0	—	—	1.89	—	12.7	—	—	1.83	—
	14.4	—	—	0.00*	—	15.4	—	—	1.79	—	13.5	—	—	1.89	—
J. R. Blockey,[4] Leathersellers Co's Technical College, London.	12.0	4 5	7.5	1.55*	1.39	—	—	—	-	—	—	—	—	—	—
	12.02	4.6	7.6	1.45*	1.40	—	—	—	—	—	—	—	—	—	—
T. A. Faust, Yocum Laboratory, Newark, N. J.....	14.0	5.0	9.0	2.10[5]	1.50[5]	—	—	—	—	—	14.9	4.7	10.2	1.95[5]	[5]1.27
	13 5	4.9	8.6	2.07[5]	—	—	—	—	—	—	15.1	5.0	10.1	1.92	—
Average soluble solids.	13.7	—	—	—	—	15.8	—	—	—	—	13.6	—	—	—	—
Average non-tannins..	—	5 1	—	—	—	—	5.5	—	—	—	—	4.6	—	—	—
Average tannins.....	—	—	8.3	—	—	—	—	10.5	—	—	—	—	9.1	—	—
Average glucose (A)..	—	—	—	2.36	—	—	—	—	2.22	—	—	—	—	2.02	—
Average glucose (B)..	—	—	—	—	1.53	—	—	—	—	1.64	—	—	—	—	1.41

NOTE—1, 2, 3, 4, 5 and (*) same as Table II.

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cept that instead of using 25 cc. of saturated neutral lead acetate, use 25 cc. of a saturated basic lead acetate solution.

SOLUBLE SOLIDS, NON-TANNINS AND TANNINS.

Determined as given in Jour. A. L. C. A., Vol. VI, No. 1, p. 12. The results received in the coöperative work are given in Tables 1, 2 and 3.

Comments of Analysts.

J. B. RAY: "It seems to make a great deal of difference whether the material is placed in the thimble loosely or tightly. A tightly packed sample left after eight hours' extraction 4 per cent. of unextracted fat. I then ran a series of extractions on the same sample which required 38 hours for complete extraction. (The results are shown in Table 4)."

TABLE 4.

(Leather tightly packed in thimble.)

Hours	Per cent.
8	25.19
10	29.09
12	29.16
14	29.21
16	29.25
18	29.28
20	29 30
22	29.32
24	29.34
32	29.40
38	29.43

"It seems to me it should be stated that the sample is to be loosely packed in the Sohxlet thimble. When loosely packed, eight hours gives complete extraction."

SOLUBLE SOLIDS.

"Some of the solutions stood for two weeks or more before they were analyzed. Certain growths appeared on the surface of the solution and a glance at the results will show you that either of the methods do not give the best results or that some change takes place in the solution on standing; I believe the latter." (Mr. Ray includes results by the alcohol method on leather No. 1 which show that the percentage of soluble solids decreases even in the presence of carbon tetrachlorid and chloro-

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form if the solution stands for several days.) "I suggest that beaker covers be used for evaporating the soluble solids solution. The tared cover is placed on the water-bath and clear solution allowed to flow slowly into it from a separatory funnel as the solution evaporates. I found that in most cases four hours were necessary for constant weight; some required six hours. The results on sugar vary enormously, due probably to the long standing of the solution before analysis."

J. M. SELTZER:—Fat Determination. The results of 6, 8, 10, and 24 hours' extraction are practically the same with leather No. 1, while leather No. 2 showed slightly higher results with 10 and 24 hours' extraction."

WATER SOLUBLE MATTER.

"In the Bureau of Chemistry method when the bath was kept at 50°, the solution in the extractor was only 45°. This method shows higher results than the official method and the solutions have a much darker color, which was due to boiling them. I also extracted the two leathers by the official method without removing the fat and found that in No. 1 the results were almost the same as those in which the fat was first removed, but with No. 2 the results were much lower when the fat was not first removed. My results with 95 per cent. alcohol are contrary to those claimed for this method. Most of the sugar is removed by eight hours' extraction. The alcohol dissolves some matter which is insoluble in water after the alcohol is evaporated off. The water solution is then very cloudy. It has been shown before that basic lead acetate gives lower results than the normal acetate and my results show the same to be true."

J. R. BLOCKEY:—Fat Determination. "By using the directed method of extraction very little is to be gained by prolonging the extraction over ten hours. Experiments were made syphoning at about ten times per hour and instead of using a thimble, the leather powder was loosely packed in the Soxhlet, in the bottom of which was placed glass wool to prevent slight particles from syphoning over. It was found that one and a half hours was sufficient to extract 29.2 per cent. of the fat from No. 2 or practically as much as is extracted in ten hours syphoning at

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the rate of four times an hour and using a thimble. On the whole, it seems preferable to extract by giving 12-15 siphonings, and if there is reason to suppose that all of the fat has not been extracted, to continue the extraction with a fresh flask. For instance, if there is reason to suspect the presence of castor oil, then petroleum ether will only slowly extract this, as the solubility of castor oil in petroleum ether is very low. By continuing the extraction with a fresh flask the castor oil would be detected. The drying of the fat residue until constant in weight is not always an easy thing, as with oxidizable oils especially oxidation may take place and thereby increase the weight, and volatilization may also take place, especially with mineral oils, and thereby decrease the weight. Perfect constancy is therefore not to be expected, and it scarcely seems fair to establish set rules and time for the extraction and drying of fatty matters, as the character of the oils and fats employed varies so considerably."

WATER SOLUBLE MATTER, A. L. C. A. METHOD.

(*Procter's Extractor was used.*)

The liquors were colorless to the end of the extraction. Experiments with American chromed hide powder gave no appreciable difference from experiments with powder chromed according to the official I. A. L. T. C. method.

Alcohol Method.—When glucose is soluble in 95 per cent. alcohol, the amount extracted in the Soxhlet apparatus may be quite considerable, considering the volume of alcohol which siphons through the apparatus in the course of the extraction. The results show that 6 out of 8 per cent. of glucose is extracted in 8 hours. Another disadvantage is the increased number of operations involved and the extra time required. Upon evaporating the alcohol resinous substances separate out. If the leather be not properly dried before the extraction, the alcohol will no longer be 95 per cent. after it has once come in contact with the leather.

By both methods.—Mineral matter is dissolved in the extraction so that both are liable to the same error unless an estimation of soluble mineral matter is made.

Glucose.—The cuprous oxid was ignited and weighed as CuO.

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It is doubtful if the advantages of using solid potassium oxalate overbalance the disadvantage of the extra time taken in determining when all the lead has been removed. The same remark applies to the neutralization of the hydrochloric acid by anhydrous sodium carbonate after inversion. The ordinary method of neutralizing the acid is quicker. Experiments were performed using the different methods, but the results showed no appreciable difference.

The results in every case are higher with the normal lead acetate than with the basic. Experiments were performed on solutions containing known quantities of glucose to determine if possible what was the cause of this higher result. It is probably due to the presence of substances like gallic acid, which reduces Fehling's solution and gives a precipitate with lead acetate which is soluble in dilute acids, such as acetic acid. By the use of basic lead acetate some of the free acid is probably neutralized so that the precipitation of gallic acid and kindred substances is more complete than with normal lead acetate. Both are liable to the same sources of error but the error in the case of normal is higher than with the basic, so that it seems preferable to use the basic. By using basic lead acetate on tannin solutions which had stood for some time and in which decomposition had taken place, the amount of glucose was very much reduced, whereas in one case by using lead acetate the amount was actually increased."

T. A. FAUST:—Fat Extraction: The 24 hour extraction seemed to give abnormal results and in my opinion 8 hours is sufficient for either sole, binding, or harness leather.

Water Extract (A. L. C. A. Method): Concordant results can be obtained provided the temperature is always kept at 50° C. A few degrees difference in the temperature, however, makes a considerable difference in the results. There is a constant breaking down of leather substances by the continued dilution with water even at different temperatures, thus making the results depend entirely upon the temperature at the time of extraction and the degree of tannage of the leather. The results are not as concordant as those by the alcohol method. The apparatus suggested for use with the Bureau of Chemistry method is rather cumbersome and difficulty in manipulation was ex-

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perienced. Constant attention was required to prevent the temperature in the water jacket from getting above 50° and it was very difficult to drive the steam through the water jacket when it was kept at this temperature because the steam was condensed. It took almost two hours before the first siphoning took place. The result on leather No. 1 is lower than with the alcohol and the A. L. C. A. method and I believe it is due to the fact that the apparatus would not siphon often enough.

Alcohol method.—There is not the breaking down of the leather substances and dissociation of tannin that there is in the water extraction methods. The tannin extracted by alcohol is, I believe, actual uncombined tannin. The leather residue after extraction with water shows a more or less dissociated and jumbled mass of leather, whereas in the alcohol method, the leather seemed to retain practically its original condition. Epsom salts are soluble in alcohol to a limited extent and I believe that this error can be ignored for commercial analyses. Glucose is quite soluble so that there is probably no advantage in the alcohol method in this respect.

Glucose.—I think that basic lead acetate gives too low results. I used sodium carbonate for neutralizing instead of potassium oxalate. When potassium oxalate was used, the results were 8.7 and 8.4 per cent. as against 7.3 and 7.5 per cent. when sodium carbonate was used. I believe the potassium oxalate preferable to sodium carbonate as it is quite difficult to know just when enough sodium carbonate is added to precipitate all the lead and not increase unduly the alkalinity of the solution. I think the method as outlined for the work on the subject is much better than the present method. The refluxing I believe to be a great improvement over the evaporating and I believe your proportion of lead acetate to the volume of solution is better than the present method calls for. Personally, I would prefer taking a little larger quantity of the solution, which would obviate the necessity of waiting so long for sufficient filtrate from which to remove the lead. The determination of glucose in the water and alcohol extractions were fairly concordant."

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COMMENT BY THE CHAIRMAN.

The results on extraction of fat are most excellent. Sample No. 1 contained approximately 2 per cent. of fat, which was entirely extracted within 6 hours. Sample No. 2, containing approximately 30 per cent. of fat was practically entirely extracted in 8 or 10 hours, and, as pointed out by several of the collaborators, it seems quite clear that if the leather is properly placed in the extractor and the siphoning of the ether is more frequent that there will be no difficulty in extracting highly greased leathers within one working day.

It would seem unnecessary to warn analysts about tightly packing materials which are to be extracted. As several, however, started astray on this point, it might be wise to expand the method to include a statement regarding the proper way to place the leather in the extractor. This statement applies as well to the water extraction of leather and tanning material, in which it now seems errors may have occurred due to packing the material in the extractor.

The committee called for "drying the fat to constant weight." The phrase "dry to constant weight" has been so long used in this country, where it is universally interpreted to mean "dry until there is no further loss in weight" that it was used in these instructions without considering that someone might misinterpret it. One analyst, at least, did so but it is unnecessary to make the present statement of the method clearer in this particular.

WATER SOLUBLE.

The results on water soluble by the A. L. C. A. method vary from 19.2 to 25.9 per cent. and average 23.5 per cent.; by the Bureau of Chemistry method (omitting one result which is clearly too low), from 22 to 25.2 per cent., averaging 24 per cent. The results by the alcohol method vary from 20.3 to 26.1 per cent. and average 24.9 per cent. The variation between the results by different workers are greatest on the A. L. C. A. method and least with the Bureau of Chemistry method. On the whole, it may be said that the results by all the methods are good but not as good as they should be by any means. But considering the unfamiliarity

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of many of the workers with one or more of the methods, they are encouraging. The soluble solids, as will be seen, average highest by the alcohol method and lowest by the A. L. C. A. method. The results on tannins and non-tannins are also very fair, the tannins averaging highest by the alcohol method and lowest by the A. L. C. A. method.

With reference to the statements so frequently made concerning the dissociation of leather substances and the removal of combined tannins, it may be pointed out that the alcohol method, against which this charge has not been made against which it is highly improbable it could hold if made, gives the highest results on soluble solids and tannins, though the results by the Bureau of Chemistry method are very close to those by the alcohol method. Personally I may say that this is a question which I have studied for a number of years most thoroughly and I have yet to find evidence of the dissociation of leather and removal of combined tannins, even on very prolonged extraction of the leather with water at 50-55° C. The results by the alcohol method are additional evidence that such removal of combined tannins does not take place. I am inclined to think that many are misled on this question by the proportionately greater removal of tannin to non-tannins in the latter stages of the extraction. This is, I think, fully accounted for by the low solubility of the reds or difficultly soluble tannins. It seems to me clear that the readily soluble tannins and the non-tannins are very quickly removed by any of the extraction processes now being studied, but it requires prolonged treatment to remove the more difficultly soluble tannins which are removed both by the water extraction method as conducted in the Bureau of Chemistry and by the alcohol method.

Several of the operators had difficulty in setting up the apparatus for the Bureau of Chemistry method. One passed the steam tube through the 50° bath, which of course should not have been done. The steam should have passed from the receiving flask directly to a condenser above the extractor, where it would be condensed and run into the extractor. One of the collaborators acknowledged his inability to set up the apparatus for the work. While it is quite clear that the alcohol method does not possess the advantages and do what

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was originally claimed for it, I am not convinced that it may not serve a useful purpose in the study of leather. We may employ it possibly to obtain more knowledge of the composition of leather and its behavior in service.

The results on glucose, when normal lead acetate was employed, were excellent, except the results of one operator whose results are fully accounted for by fermentation. The results by the alcohol method are not so concordant and often not so high as when determined by the water extraction method. This is probably due to insufficient extraction on the part of several of the collaborators.

The results with basic lead acetate average approximately 1½ per cent. lower than by the normal lead acetate. The results by normal lead acetate agree very closely with the theoretical amount of glucose present in and added to the leather. The use of normal lead acetate has received in the past few years so much careful attention and has so generally replaced the basic salt in clarification of sugar solutions that there can be but little if any doubt as to the advisability of employing the normal salt on tannin solutions and until someone presents positive data to the contrary, I think we are bound to use it. In my own laboratory a very careful study of the two salts on tannin soutions has been made, on tanning solutions containing sugars as well as on solutions containing practically no sugars. As on numerous solutions containing no sugars there was no difference in the results between the two lead solutions I am not prepared to give much consideration to Mr. Blockey's preference for the basic acetate.

With reference to extraction it may be again remarked that it is a well known fact that the removal of soluble matter is not insured by stating the time of extraction. Neither is it entirely controlled by the speed with which the solvent passes through the material, though within limits it is probably more affected by rapid percolation than by prolonging the total time of extraction. The busy chemist, however, cannot note each time an extractor syphons, or watch constantly the speed of percolation. It is quite customary therefore to state the time for which the extraction should be conducted, this time being what experience has shown to be ample. The question is one that

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has been before the Association several times and the attempt has been made to state as far as practicable the rate and time of extraction. This should be done in the method for fat.

RECOMMENDATIONS

Fats:—In the sentence after leather insert, "placed loosely."

At the end of the first sentence insert, "syphoning should occur at least six times per hour and continue six to ten hours with leather containing much grease."

Glucose:—Change first paragraph to read: "(a) To 200 cc. of the extract add 25 cc. of a saturated solution of normal lead acetate, mix thoroughly, allow to stand about 15 minutes, and filter. The funnels and beakers must be kept covered to prevent evaporation. Remove the lead from the filtrate by adding a slight excess of solid potassium oxalate and filtering. Pipette 150 cc. of the last filtrate into a 600 cc. Erlenmeyer flask and add 5 cc. of concentrated HCl and boil under a reflux condenser for two hours, cool, neutralize with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (This filtrate must be clear.) Use 50 cc. of this filtrate for the determination of sugar."

The methods for the analysis of leather give satisfactory results when carefully executed. It is recommended therefore that in future, in addition to further work on some of the regular determinations, something be done toward the identification of the various kinds of greases, and water soluble materials found in leather, and also that methods for the detection and determination of free mineral acids in leather be studied.

REPORT OF COMMITTEE ON ACIDITY OF TAN LIQUORS.

By L. Balderston.

Much has been published on this subject during the year by European investigators. The electrometric method for the measurement of acidity has received much attention. Results of this work are shown in the abstract of Sorensen's monograph, in the March, April and May numbers of the JOURNAL for the

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current year, and in the articles by Sand, Law and Wood in the March and September numbers. The subject of the effect of acids in the tanning process is dealt with in Procter's paper on "Colloid Chemistry and Tanning" in the January number, and in "Acids in Tan-Liquors" by Procter and Seymour-Jones in the February number. Another important paper appeared in the June number, "On the Action of Dilute Acids and Salt Solutions upon Gelatine," by Henry R. Procter. In the September number appeared Procter's article on "Strength of Acids," from the Tanner's Year-book, and from the same source in the November issue, "The Natural Acids of the Tan-Liquors and their Influence in Leather Manufacture," by R. Arnold Seymour-Jones.

The modern modes of investigation of acidity require apparatus which has not up to the present been at the command of any of the members of the committee, so that nothing of the kind has been attempted.

Work has been done on only two topics, the use of antiseptics to prevent loss of acid, and the proper proportion of gelatine to be used in precipitating tannin. Preliminary work indicated that thymol and tar camphor might be used for preventing loss of acid. A set of samples collected over a period of two weeks were taken in duplicate, one set with thymol added and one without. The results of this experiment are shown in Table I, per cent. acid as acetic. The liquors are given in order of

TABLE I.

Liquor	With thymol		Without thymol	
	New	Sapped	New	Sapped
1	0.78	0.96	88	78
2	0.70	0.86	76	74
3	0.74	0.88	72	66
4	0.70	0.88	64	62
5	1.00	0.98	76	66
6	—	0.84	—	66
7	—	0.52	—	44

strength, numbers 6 and 7 being handler liquors. A study of this table shows that the sapped liquors without thymol are all lower, while the stronger new ones are higher without thymol than with it. It had appeared more than a year ago that in certain liquors when protected from the air the acid tended

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to increase, and the thymol, by discouraging the acid—forming bacteria probably prevented the increase which took place in the untreated new samples of liquors 1 and 2.

A set of bottles had been filled with new liquor from the same tannery on May 20, 1910. At that time the total acidity was 0.82 per cent., 0.44 per cent. of which was volatile. All of these bottles but one were sealed. In the open vessel the volatile acid disappeared much more rapidly than the non-volatile, while in the closed vessels the total increase in the two was about proportional. Results are given in Table II, per cent. acid as acetic.

TABLE II.

Date 1910	Closed samples			Open samples		
	Vol.	Non-vol.	Total	Vol.	Non-vol.	Total
May 20.....	0.44	0.38	0.82	0.44	0.38	0.82
May 27.....	0.48	0.37	0.85	0.04	0.21	0.25
June 7.....	0.48	0.36	0.84	0.02	0.17	0.19
June 15.....	0.49	0.41	0.90	—	—	—
July 18.....	0.60	0.40	1.00	—	—	—
Aug. 26.....	0.57	0.50	1.07	—	—	—
Oct. 5.....	—	—	1.06	—	—	—
1911						
Nov. 13.....	—	—	1.07	—	—	—

In another preliminary experiment twelve equal samples of the same liquor, acidity 0.675 per cent., were placed in open bottles. To one was added 0.02 per cent. thymol, to another 0.035 per cent. and to a third 0.05 per cent. "Tar camphor," 0.025 per cent. was added to a fourth, 0.05 per cent. of the same to a fifth and 0.1 per cent. to a sixth. These were placed in a basement room where the temperature ranged from 19° to 21° C. Another set prepared in the same manner were placed in an incubator and kept between 32° and 35° C. At the end of two weeks both sets were examined. Those kept in the cold showed no loss. Those kept in the incubator gave the following results: Thymol 0.02 per cent., 0.6 per cent. acid, thymol 0.035 per cent., 0.67 per cent. acid, thymol 0.05 per cent., 0.67 per cent. acid; tar-camphor 0.025 per cent., 0.50 per cent. acid, tar-camphor 0.05, 0.59 per cent. acid, tar-camphor 0.1 per cent., 0.67 per cent. acid.

The thymol samples were examined after four weeks, and the acid was found to be falling off. This loss seems to be due

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to an organism which forms a red film on the surface. It is not a yeast, the individuals being much smaller, and round instead of elongated. Further addition of thymol prevents the growth of this film and holds up the acid for a longer period. Two samples treated with about 0.1 per cent. thymol ten weeks ago still have no growth, and the acid content is almost unchanged.

These results seemed to indicate that thymol or tar camphor might be used to advantage as a preservative. Careful tests showed that neither influenced the tannin content of the liquors as shown by analysis. The following directions were accordingly sent to several members of the committee:

"Select a liquor known to contain a considerable proportion of acid. Divide this into three portions of at least 300 cc each. To one of these portions add one fiftieth per cent. thymol and to another one-twentieth per cent. of the substance sold by the stores as tar camphor. Let the three samples stand open and test the total acidity at the beginning, and at the end of one week, two weeks, three weeks and four weeks. Note the temperature during the experiment and report in connection with your results." The results sent in are given in Tables III, IV and V. (Per cent. acid as acetic.)

TABLE III.—C. R. OBERFELL.

	New	1 week	2 weeks	3 weeks	4 weeks
Straight liquor	0.74	0.40	0.28	0.22	0.19
1/50 per cent. thymol	0.74	0.52	0.38	0.29	0.24
1/20 per cent. naphthalene	0.74	0.67	0.44	0.34	0.22

All results average of two determinations. Temperature varied from 21° to 35° C. Liquor containing naphthalene the only one on which no film formed. The thymol used was free from acid. Each liquor brought to original volume before determination was made.

TABLE IV.—J. M. SELTZER.

	Start	1 week	2 weeks	3 weeks	4 weeks
No preservative	0.68	0.57	0.45	0.32	0.23
1/50 per cent. thymol	0.68	0.77	0.62	0.45	0.29
1/20 per cent. tar camphor	0.68	0.59	0.55	0.42	0.28
1/20 per cent. oil of mustard	0.68	0.67	0.69	0.67	0.68

Sapped liquor used; barkometer 30°. Temperature from 70° to 90° F.

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TABLE V.—L. BALDERSTON.

	Start	1 week	2 weeks	3 weeks	5 weeks
No preservative	1.08	0.86	0.66	0.51	0.32
1/50 per cent. thymol	1.08	1.07	1.07	—	0.52
1/50 per cent. tar camphor	1.08	0.82	0.59	0.46	0.28
1/20 per cent. tar camphor	1.08	0.84	0.57	0.53	0.22

Temperature during experiment 18° to 25° C. All results mean of two or more titrations. Loss by evaporation made up before each determination.

Mr. Seltzer's results with oil of mustard were so good that the writer set two liquors with 1/20 per cent. of oil of mustard (volatile) and two blanks, in an incubator where they were kept at 30° C. Results in Table V.

TABLE V.

	Start	3 days	7 days	10 days
Liquor 1, blank	0.46	0.38	0.25	0.19
Liquor 1, 1/20 per cent. mustard oil....	0.46	0.43	0.28	0.20
Liquor 2, blank	0.52	0.44	0.40	0.35
Liquor 2, 1/20 per cent. mustard oil....	0.52	0.52	0.42	0.37

The volume was made up to replace evaporation each time before determination was made. These results seem to indicate that oil of mustard does not hold the acid well at high temperatures.

The percentage of naphthalene used in the collaborative work was evidently too small to be efficient. Naphthalene is very slightly soluble in cold water, probably not more than 1/200 of 1 per cent. It is quite possible that when undissolved it hinders the growth of the yeasts which destroy acid. It is also quite possible that tan liquors dissolve more of it than pure water. Whatever the explanation, its presence in liquors to the amount of 0.1 per cent. seems effective in preserving the acid for two weeks. It is less satisfactory than thymol, in that it gives a disagreeable odor to the liquors, and it seems less reliable in its results. In regard to oil of mustard, the writer does not feel qualified to speak. Mr. Seltzer testifies that in the proportion of 1/20 per cent. it gives good results in practice.

The other point taken up by the committee was suggested by some opinions expressed in the convention last year in regard to the quantity of gelatine proper to be used in precipitating tannin from solutions to be tested for acid. In order to obtain

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data which might throw some light on this point, the following directions were sent to several members of the committee:—

"Select a liquor strong in tannin, preferably about 5 per cent. and having an acidity of not less than 0.5 per cent. Dilute a portion with an equal volume of water, and another portion with 3 times its volume of water.

Take 25 cc. of the original liquor and the same quantity of each dilution, and add to each 50 cc. of a 1 per cent. water solution of gelatine. Make up to 250 cc., add 5 grams of kaolin, shake and let settle for at least one hour. Titrate 30 cc. of the supernatant liquor with N/10 NaOH, using hematin indicator.

With 3 other portions of 25 cc. each, precipitate the tannin with 25 cc. of 1 per cent. gelatine and proceed as before.

Take another 25 cc. of the 1 to 4 dilution and precipitate with 12.5 cc. of the gelatine and proceed as before.

Please make each titration in duplicate; *i. e.*, titrate two 30 cc. portions from each vessel."

It was thought that the three liquors thus prepared, having acid in the ratio of 4:2:1 would afford a test of the proper amount of gelatine to use. Results are given in Tables VI, VII VIII and IX, in per cent. of acid as acetic. Undiluted liquor, No. 1, 1:2, No. 2, 1:4, No. 3.

TABLE VI.—C. C. SMOOT.

Oak liquor, 5.22 per cent. tannin.

	1	2	3
50 cc. gelatine	0.553	0.278	0.142
25 cc. gelatine	*	0.267	0.138
12.5 cc. gelatine	—	—	0.160

* Unable to titrate on account of dark color.

TABLE VII.—JOHN H. YOCUM.

	1	2	3
50 cc. gelatine	0.35	0.115	0.045
25 cc. gelatine	0.40	0.135	0.04
12.5 cc. gelatine	—	—	0.055

TABLE VIII.—L. BALDERSTON.

Oak liquor, 5.1 per cent. tannin.

	1	2	3
50 cc. gelatine	0.95	0.44	0.23
25 cc. gelatine	0.99	0.48	0.22
12.5 cc. gelatine	—	—	0.26

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TABLE IX.—F. O. SPRAGUE.

	1	2	3
50 cc. gelatine	0.61	0.26	0.12
25 cc. gelatine	0.68	0.31	0.13
12.5 cc. gelatine	—	—	0.16

Mr. Sprague says: "Results indicate an appreciable loss of acid with larger amounts of gelatine, but I should not be in favor of smaller amount for liquors of this strength, as the error is more or less neutralized by greater ease of titration and clearer end point. Possibly a sliding scale could be adopted."

Mr. Smoot says "We are of opinion that the amount of gelatine to be added to any tannin solution cannot be fixed at a definite quantity, but should vary with the amount of tannin in the solution. In practice we always add sufficient gelatine to form a white emulsion and take this as the point showing complete precipitation of the tannin. This point can be recognized with a little practice."

The writer's experiments indicate that 10 cc. of a 1 per cent. gelatine solution for 1 per cent. tannin content in the liquor is a sufficient quantity to precipitate all the tannin from 25 cc. and that with a less quantity than this it is not practicable to get good results. With most liquors a greater quantity of gelatine causes the liquid to settle more rapidly and gives a clearer supernatant liquor.

The writer tried another experiment, varying the procedure by making up the liquors to the same acidity. A liquor analyzing 8.8 per cent. tannin and 0.66 per cent. acid as acetic was diluted to one-half, one-fourth and one-eighth. Acetic acid was added so as to make up the acidity of each to 0.66 per cent. The acidity was then determined, first by precipitating 25 cc. of each with 50 cc. gelatine, and second by using gelatine proportional in amount to the tannin content. It will be observed from the results (Table X) that except when the quantity of gelatine used was too small to precipitate all the tannin, the indicated quantity of acid in all the liquors was practically the same. The liquors numbered in order of tannin strength 1, 2, 3 and 4, and results are in per cent. acid as acetic.

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TABLE X.

	1	2	3	4
50 cc. gelatine	0.70	0.63	0.60	0.60
80 cc. gelatine	0.60	—	—	—
40 cc. gelatine	—	0.62	—	—
20 cc. gelatine	—	—	0.61	—
10 cc. gelatine	—	—	—	0.61

In regard to the use of preservatives, it is hard to draw any satisfactory conclusions from the collaborative work. The chairman believes that thymol in a proportion as great as 1/20 per cent. will be found satisfactory in all cases where liquors are not kept longer than one month. It is very desirable to have more experiments on this subject in the collection of tannery samples, so that it may be decided what is the best preservative to use, and what percentage of it should be added.

REPORT OF THE COMMITTEE ON OILS AND FATS.

By Charles R. Oberfell.

The Committee on Oils and Fats this year confined its work to the examination of methods for the analysis of mineral leather oils, it being conveyed to the chairman that this was the special line of work you wished investigated.

The secretary sent the names of the following men who had signified their desire to serve on this committee:—P. A. Esten, G. W. Priest, I. C. Bull, W. K. Alsop, A. G. Stilwell, T. D Simpson, F. W. Alden, C. A. Reisig and F. O. Sprague. Of these, Messrs. Alsop, Simpson and Sprague undertook the work, Mr. Bull asked to be excused and the others failed to reply to the preliminary communication.

On account of this limited size of the committee the work is necessarily of a less convincing character, which fact the chairman regrets.

The preliminary letter to the committee asked for opinions on the present methods of Oil and Fats analysis, also for suggestions as to new lines of investigation. This elicited a general condemnation of the present methods. For illustration Mr. Alsop wrote that "Methods just as good, or better than the ones we have can readily be obtained from standard books

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on the subject. It may be convenient to have such methods if they are revised and kept up to date. Under "acid value" I note the use of alcohol potash is specified. I have never used an alcoholic solution for this determination, and have never had any trouble getting good results. I believe it is a disadvantage rather than otherwise." It seemed to be the idea that we should have methods for testing the specific oils used in the leather industry as, Sod Oils, Moellons, Wool Grease, Sulfonated Oils, Mineral Oils etc., and not to have general methods for the determination of saponification value, iodine number, etc.

From the replies it was decided to center attention on Mineral Oils for this year and leave the other oils and fats for subsequent committees.

In selecting tests for mineral oils care was taken to exclude any tests the result of which would be of doubtful value in deciding on the merits of the oil under examination. Accordingly the gravity, viscosity, reaction, carbon and tar, purity, emulsification and evaporation were selected. In drawing up methods for these tests an effort was made to select the simplest apparatus possible in order that, on account of low cost, all laboratories could be fully and uniformly equipped. The selection of a viscosimeter was the most perplexing, but for trial the Dudley Viscosity Pipette (standardized to deliver 100 cc. of water at 100° F. in 35 seconds) was decided upon. This is a simple and cheap apparatus and is satisfactory at low temperatures, which is all that is required for leather oils.

Two samples of mineral oil were sent out with the following directions:

SPECIFIC GRAVITY.

Cool the oil to 15.5° and place in a water-bath at this temperature during balancing. Use a Westphal balance and see that it is in standard condition before use.

EVAPORATION TEST. (a)

Weigh approximately 0.5 gram of oil into a flat bottom glass dish (crystallizing pattern) 1½ in. diameter. Place in a drying oven the temperature of which is constant at 60-65° and heat for

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8 hours. Cool in desiccator and weigh. Calculate the loss in per cent.

(b)

Weigh 1.0 gram of oil into a flat bottom crystallizing dish 2 ¾-3 in. diameter and heat in drying oven at 95-100° for 16 hours. (This is arranged so that evaporation may proceed during the night.)

VISCOSITY.

Use a Dudley's Viscosity Pipette for this work. It is graduated to deliver 100 cc. of water at 100° F in 35 seconds.

Test the pipette with water at 20° C and report in seconds in connection with other results.

Bring the oil to 20°, and work in a room at 20° if possible. If not report temperature of room with results. Allow the oil to flow and record number of seconds required.

REACTION OF OIL.

Heat about 15 cc. of the oil with 50 cc. distilled water in a test tube. Draw off the water and test its reaction with a solution of litmus. With methyl orange or phenolphthalein if Litmus is not at hand.

ASPHALTIC BASES AND TAR.

Place 5 cc. of the oil in a separatory funnel of about 200 cc. capacity. Add 95 cc. gasoline 84-88° (petroleum ether). Shake well and run into a 100 cc. graduated cylinder. Allow to stand 15 minutes. Report volume of precipitate.

PURITY.

Report any turbidity or presence of solid particles of extraneous matter.

EMULSIFICATION TEST.

Place 50 cc. of oil in a 100 cc. graduated cylinder and add 25 cc. distilled water. Stopper tightly and shake vigorously for 2 minutes. This will form the emulsion. Note the extent of emulsification as—Good. Medium. Poor. Also length of time until the emulsion breaks as indicated by appearance of a water layer about 5 cc. deep.

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TABLE I.

	Gravity	Evaporation a. %	Evaporation b.	Viscosity seconds	Reaction	Carbon and tar bases	Purity	Emulsification
Sample "A."								
Alsop	0.8625	10.54	22.61	56 1/5 [4]	Acid	None	Very slight sediment	Good—8 min.
		11.48	21.63					
		11.60	15.34 [1]					
			11.29 [2]					
			10.28 [3]					
Oberfell	0.8630	4.25	30.66	56 1/5 [5]	Acid	None	Very turbid	Poor—5 min. No foam.
		4.36	26.72					
Simpson	0.8615	—	—	50 [6]	Neutral	None	Clear	Good—5 min.
Sample "B."								
Alsop	0.8706	0.27 [7]	0.22	191 4/5 [4]	Neutral	None	Clear	Good—17 min.
		0.28	0.22					
		0.23	0.25					
			0.15					
Oberfell	0.8715	0.04	0.49	194 4/5 [5]	Neutral	None	Clear	Good—120 min. Foam.
		0.03	0.48					
Simpson	0.8690	—	—	137 2/5 [6]	Neutral	None	Clear	Medium—3 min.

[1] 1.5 grams. [2] 2.0 grams. [3] 2.5 grams. [4] Viscosimeter at 20° C.—33 2/5 seconds. [5] Viscosimeter at 20° C.—35 seconds.
[6] Viscosimeter at 20° C.—35 1/5 seconds. [7] Gain.

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TABLE II.

Dish 1½″ diameter. 8 hours at 60-65° C.

Oil	% loss 1	% loss 2	% loss 3
A	9.98	9.04	11.28
B	0.12	0.20	0.33

Dish 2¾″ diameter. Oven 16 hours.

Oil		Weight 1 gr.	Weight 1 gr.	Weight 1.5 gr.	Weight 2 gr.	Weight 2.5
A	1st	30.08	30.09	25.06	21.37	15 67
	2d	20.08	20.06	20.12	15.95	13.49
B	1st	no loss	0.18	0.31	0.19	0.22
	2d	0.19	0.15	0.12	0.14	0.02

Dish 1½″ diameter. Heating 2 hours at 100°C.

Oil 1 gr.		1st 2 hrs.	2d 2 hrs.	3d 2 hrs.	4th 2 hrs.	5th 2 hrs.	6th 2 hrs.	7th 2 hrs.
A	1st	15.11	26.81	40.81	47.98	53.92	—	—
	2d	21.68	39.59	49.00	53.65	59.44	63.48	65.49
B	1st	00.28[1]	00.07[1]	00.17	00.71	1.50	1.82	2.00
	2d	00.34[1]	00.52	1.00	1.19	1.54	1.68	1.62

Dish 2¾″ diameter. 2 hours at 100°C.

Oil 1 gr.		1st 2 hrs.	2d 2 hrs.	3d 2 hrs.	4th 2 hrs.	5th 2 hrs.	6th 2 hrs.	7th 2 hrs.
A	1st	36.06	52.32	56.62	59.79	66.84	69.33	70.84
	2d	28.72	41.59	51.72	56.76	61.89	65.98	69.00
B	1st	00.35[1]	00.90	1.65	2.12	3.05	3.31	3.69
	2d	00.06[1]	00.51	00.81	1.00	2.08	2.00	2.08

[1] Gain.

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The cause for such results as in the evaporation test, is hard to explain. Mr. Alsop suggests that it may be due to "non-homogeneous mixtures or differences in the surface exposed during heating." Mr. Alsop made a special examination on the evaporation test, which results are given in Table II.

Possibly the flash test would give as good an indication of the amount of volatile matter as the evaporation with comparable results. Accordingly another sample "C" was sent out with the following directions for the determination of the flash point.

"Set a porcelain crucible 60 mm. top diameter, 25 mm. bottom diameter and 50 mm. in height (any open cup of approximately this size will serve) in a sand bath so that the top is below the rim of the bath. Fill the cup to within ¼ inch of the top, adjust the thermometer in the center of the liquid. Apply heat so that the temperature rises 8° per minute and apply test flame first at 150° and then at every rise of 2.5°. Use a jet flame approximately 8 mm. long and 3 mm. in diameter. Apply the flame by passing slowly and completely across the cup about ½ inch above the level of the oil and just in front of the thermometer."

The only disadvantage when working with the flash point is that for oils coming from different crudes it is necessary for the analyst to know the range for each separate class, while with the evaporation test any definite loss represents just so much for all classes of oils.

As to the viscosity it seems that it is difficult to obtain instruments which are all graduated to flow the 100 cc. in the same time. Possibly any apparatus house would guarantee to supply standard pipettes, which would solve the difficulty and put all on an even basis. It also seems that the pipette has an inherent fault in that as the oil drains from the tip it greatly magnifies the real viscosity of oils high in this characteristic. An improvement in the Dudley Pipette would be to have two marks, one above and one below the bulb, between which the 100 cc. is contained, the time to be noted as the oil passes the two marks. This would eliminate taking the time while the oil drips from the tip.

Since the foregoing was written the time has expired for this report to be in. Mr. Sprague failed to report in time although he had hoped to do so, but was deterred by putting a new

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TABLE III.—SAMPLE "C."

	Gravity	Evaporation % a.	Evaporation % b.	Viscosity seconds	Reaction	Carbon and tar bases	Purity	Flash point	Emulsification
Alsop.....	.8647	0.98	7.07	97-2/5 [1]	Neutral	None	Small	190°	Medium [3]
		0.91	6.73				number		32 seconds
		1.03	6.94				solid		to break
		0.79	6.55				particles		1 cc.
		0.76	6.72						
		Average	Average						
		0.89	6.80						
Oberfell	.8649	1.04	9.29	98 [2]	Neutral	None	Clear	195°	Good
		1.05	8.60						20 minutes
									no foam

[1] Viscosimeter at 20° C.—33-2/5 seconds. Room temp. 21°.

[2] Viscosimeter at 20° C.—35 seconds.

[3] Used 12 cc. oil and 6 cc. water.

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laboratory in order. The results are not complete enough to draw any definite conclusions and the best that can be said for this report is that it clears up the way for more substantial work next year.

Valuable information can be obtained from an emulsification test. The method tried out was worked up in my laboratory, but it failed to give concordant results in the hands of different observers. It has been of definite value to me, but only by having an oil of known emulsifying power with which to compare the unknown sample.

It could not be the province of this committee to specify definite values for mineral oils, although such probable specifications were freely discussed by some of the committee. This is a matter to be left with each chemist and it is only experience with leather oils that will enable anyone to say, from the analysis, whether an oil will be suitable for a certain class of work.

THE ACTION OF AIR UPON LIME.

Louis E. Levi and August C. Orthmann.

As the tanning industry has advanced, the materials which were formerly looked upon as being indispensable have gradually been eliminated and salable leathers are being produced without the use of those materials which were then looked upon as absolutely necessary for the manufacture of good stock.

Among the few materials which have not as yet been affected by the progress of scientific tanning, lime remains as a factor.

The lump lime now used is open to a great objection on account of the grit contained, by being imperfectly burned, and the rapid air slaking property.

The grit is liable to scratch the grain thereby putting the finished leather into a lower class and consequently causing loss to the tanner.

The air slaking property of lump lime also causes a loss by reducing the amount of available lime (CaO).

The hydrated lime now placed upon the market is apparently free from these objections.

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TABLE I.—Relative Humidity.

Temp. of room °F.....	—	70	63	63	63	72	70	75	70	76	—	67	66	63
Per cent. humidity	—	50	48	61	52	52	53	45	52	38	—	42	62	57
Hours when taken	24	48	72	96	120	144	168	192	216	240	264	288	312	336

TABLE II.—Lump Lime After Exposure.

Per cent. CaO and $CaCO_3$ present.

Length of time exposed, hours	48	96	144	192	240	288	336
Per cent. available CaO	82.257	73.608	65.965	63.661	62.406	62.406	57.327
Per cent. $CaCO_3$	3.27	2.337	12.153	15.893	16.117	16.08	17.763

TABLE III.—Powderred Lump Lime After Exposure.

Per cent. CaO and $CaCO_3$ present.

Length of time exposed, hours	48	96	144	192	240	288	336
Per cent. available CaO	77.325	68.90	63.033	62.30	59.473	59.473	57.588
Per cent. $CaCO_3$	4.30	7.479	15.893	16.293	19.857	19.819	22.437

TABLE IV.—Hydrated Lime After Exposure.

Per cent. CaO and $CaCO_3$ present.

Length of time exposed, hours	48	96	144	192	240	288	336
Per cent. available CaO	62.828	54.552	50.782	47.222	46.594	41.882	35.60
Per cent. $CaCO_3$	14.49	25.017	30.402	36.111	36.647	41.06	49.324

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TABLE V.—COMPARISON OF AVAILABLE LIME LOST.

Hydrated lime 69.577 per cent. CaO in original. Lump and powdered lime 95.282 per cent. CaO in original.							
Length of time exposed, hours	48	96	144	192	240	288	336
Hydrated lime, per cent. available CaO lost	6.749	15.025	18.795	22.355	22.983	27.695	33.977
Lump lime, per cent available CaO lost	13.025	21.674	29.317	31.621	32.876	32.876	27.955
Powdered lump lime, per cent. available CaO lost	17.957	26.382	32.249	32.982	35.807	35.807	37.694

TABLE VI.—COMPARISON OF $CaCO_3$ GAINED OVER THAT ORIGINALLY PRESENT.

Length of time exposed, hours	48	96	144	192	240	288	336
Hydrated lime, per cent. $CaCO_3$ gained	121.42	282.29	364.58	451.82	460.02	527.45	653.73
Lump lime, per cent. $CaCO_3$ gained.....	*26.35	*47.36	173.71	257.95	263.00	262.16	300.06
Powdered lump lime, per cent. $CaCO_3$ gained ...	*3.15	68.45	257.95	266.96	347.23	346.37	405.34

* Loss.

TABLE VII.—COMPARISON OF THE LOSS OF AVAILABLE CaO OF THE LUMP, POWDERED LUMP AND HYDRATED LIMES FIGURED TO 100 PER CENT. AVAILABLE CaO BASIS.

Length of time exposed, hours	48	96	144	192	240	288	336
Hydrated lime, loss per cent. available CaO	9.70	21.59	27.01	32.13	33.03	39.80	48.83
Lump lime, loss per cent. available CaO	13.67	22.75	30.77	33.18	34.50	34.50	39.83
Powdered lump lime, loss per cent. available CaO	18.85	27.69	33.85	34.62	37.58	37.58	39.56

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On account of the difficulty of obtaining data on the action of the air upon lime it was of great interest to us to carry out experiments for the comparison of the air action on hydrated, lump and powdered lump lime.

The analysis of the lump, hydrated and powdered lump lime which we took for our experiments is as follows:—

Lump lime.	
CaO (available)	95.282 per cent.
$CaCO_3$	4.440 per cent.
Hydrated lime.	
CaO (available)	69.577 per cent.
$CaCO_3$	6.544 per cent.
Powdered lump lime	
CaO (available)	95.282 per cent.
$CaCO_3$	4.440 per cent.

Duplicate samples of the above limes were taken and weighed into open glass dishes of about 4 inches in diameter and ½ inch deep. Each dish containing 30 grams of material spread evenly on the bottom and allowed to stand open for 48 to 336 hours. A sample dish taken every 48 hours and analyzed.

The humidity and temperature of the room taken every morning. The humidity was taken with a Johnson Whirling Hygrometer. Tables I to VII are the results of our investigation:—

From the tables it will be seen that the hydrated lime loses less than the lump and powdered lump on available lime by exposure to moist air for the time of the different exposures up to the 240 hour period inclusive. It will also be seen that the apparent loss of $CaCO_3$ in the lump and powdered lump lime is due to the absorption of water before the carbon dioxide of the air begins to convert the oxide to carbonate.

The powdered lump lime naturally takes up moisture and carbon dioxide quicker than the lump lime on account of the greater area exposed.

Leaving the cost of the different limes out of the question, the lump lime has its advantage by resisting the action of the air for a longer period, then again a great disadvantage is the amount of grit as above stated and the liability of burning the

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lime while slaking, for as simple as this operation appears it should not be neglected for many a good lime is spoiled in the slaking.

Laboratory of Pfister and Vogel Leather Co.,
Milwaukee, Wis.

THE CALIFORNIA TAN-BARK OAK.

This is the title of Bulletin 75, Forest Service, U. S. Department of Agriculture, issued Sept. 20, 1911. It is a pamphlet of 34 pages, consisting of 3 parts. The first paper is by Willis Linn Jepson, "Tanbark Oak and the Tanning Industry." It is to a large extent the same as the paper by the same writer published in this JOURNAL, Vol. II, p. 197. It is estimated that there are now standing 1,425,000 cords of bark in California and Oregon, a supply sufficient for about 50 years at the present rate of consumption. The cord is commonly determined by weighing, 2,400 lbs. of freshly peeled bark or 2,300 lbs. of bark stacked for one year being considered a cord. Many second-growth crops have now been harvested, the quality averaging rather lower than that from older trees. The percentage of tannin in the bark varies with the distance from the ground, as shown in table I.

TABLE I.

Location of sample	Thickness inches	Tannin per cent.	Non tans. per cent.
Rump	1 7/8	29.20	12.86
First cut	1 7/8	25.77	12.72
15 feet	1 5/8	19.93	10.76
31 feet	1 3/8	16.13	9.26
45 feet	3/4	19.37	11.63
60 feet	1/2	13.16	9.40
66 feet	5/16	13.21	8.17
74 feet	3/16	10.00	6.78
78 feet	1/8	12.50	9.42
84 feet	1/16	10.82	8 42

Table II gives analyses of bark from various localities.

Analysis of bark from three second-growth trees gives average tannin content 16.20 per cent., non-tans 9.27 per cent., reds 0.69 per cent. A table of analyses of barks from various other California trees is given. (Table III.)

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TABLE II.

Locality, etc.	Tannin per cent.	Non-tans. per cent.	Reds per cen
Briceland, Humboldt Co., thick bark	24.74	13.18	3.08
Acorn Region, Humboldt Co., thick bark	14.82	9.60	1.78
Acorn Region, Humboldt Co., thin bark	14.90	11.86	2.16
West of Ukiah 1½-foot tree, 3 feet from ground	15.60	7.12	2.52
West of Ukiah 1¾-foot tree	15.36	10.02	1.88
West of Ukiah, east of Coast Range Summit	20.51	11.21	3.24
Elk Creek, Mendocino Co., thick bark	22.20	11.69	2.87
Elk Creek, Mendocino Co., medium bark	14.92	8.89	1.15
Elk Creek, Mendocino Co., thin bark	14.00	6.73	1.86
Near coast at Kenney's, 2-foot tree	22.73	10.07	1.14
Near coast at Kenney's, 2-foot tree in open	16.20	8.92	3.76
Half Way House, Ukiah-Mendocino Road, 2-foot tree on south slope exposed to sun	19.08	9.76	7.96
San Vincente Creek, Redwood district, 3-foot tree, smooth	21.61	6.85	2.14
San Vincente Creek, Redwood district, 2½-foot tree, rough	18.93	5.40	2.67
San Vincente Creek, Redwood district, 3½-foot tree	18.24	9.24	3.60
Average	18.26	9.37	2.79

The wood is excellent for fuel, burning with little smoke and little ash. The tannin content of the wood is very small. More than nine-tenths of the wood so far peeled has been wasted, owing to difficulties of transportation. Mr. Jepson summarizes the result of his study of the tanbark oak as follows:—

(1) The bark of tan-bark oak is one of the most valuable tanning agents known for the production of heavy leather. Bark from the interior ridges and southern districts is prized more than bark from the deep redwood belt or from northern districts, because it averages higher in tannin.

(2) The Pacific coast tan-bark oak belt contains enough standing tan-bark at the present time to supply the needs of California tanneries at their present rate of consumption for 47 years.

(3) There should be more systematic methods in peeling and a greater proportion of the bark above the clear trunk should be taken. Bark from one-half to one-fourth inch thick should be saved whenever possible. Chipped bark should be sacked before bunching the coil bark. Trees with bound bark should be temporarily passed, and not mutilated or sacrificed. Tops should be burned in the winter following cutting to prevent the destruction of young growth and of passed trees by wild forest fires.

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TABLE III.

Species	Locality	Tannin per cent.	Non-tannins per cent.	Reds per cent.
California black oak (*Quercus californica*)	Vaca Mountains, Solano County	10.00	10.25	0.95
California black oak	Briceland, Humboldt County	10.16	7.88	0.32
California live oak (*Quercus agrifolia*)	Berkeley	18.76	9.40	1.48
Highland oak (*Quercus wislizena*)	Vaca Mountains, Solano County	7.92	5.88	1.20
Highland oak	Southern Mendocino	6.67	2.83	1 64
Canyon live oak, maul oak (*Quercus chrysolepis*)	Vaca Mountains, Solano County	12.18	10.18	0.80
Canyon live oak	South Central Mendocino	6.56	5.19	1.00
California white oak (*Quercus lobata*)	Visalia	11.97	11.28	1.55
Pacific post oak (*Quercus garryana*)	Southern Humboldt	7.07	4.93	0.36
Pacific post oak	South Central Mendocino, "Bald Hills,"	6.20	4.16	1.00
Western Chinquapin (*Castanopsis chrysophylla*)	Southern Humboldt	7.60	4.34	0.64
Red alder (*Alnus oregona*)	Mendocino coast	8.60	12.00	1.68
California yellow willow; western black willow (*Salix lasiandra*)	Berkeley	1.45	3.09	0.00
California laurel (*Umbellularia californica*)	Briceland	15.58	10.46	0.97
Monterey pine (*Pinus radiata*)	Berkeley (cult.)	14.11	2.85	2.60
California swamp pine (*Pinus muricata*)	Mendocino coast	13.45	3.99	3.72
Lowland fir (*Abies grandis*)	Mendocino coast	9.03	4.59	0.74
Sitka spruce (*Picea sitchensis*)	Mendocino coast	17.52	6.24	1.60
Douglas fir (*Pseudotsuga taxifolia*)	Southern Humboldt	7.15	5.25	0.42
Western hemlock (*Tsuga heterophylla*)	Mendocino coast	10.80	3.46	1.32
Western hemlock	Noyo River, Mendocino coast	14.40	6.56	2.42
Redwood (*Sequoia sempervirens*) bark	Mendocino coast	2.50	2.74	0.10
Redwood, sapwood	Mendocino coast	1.76	5.72	0.59
Redwood, heartwood	Mendocino coast	3.91	5.85	1.58

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(4) Tan-bark oak is surpassed in reproductive powers by no other forest trees in western America, except the redwood, and it stands very close to that species. A crop of sprouts will normally arise from the base of every peeled stump. In order to favor this crop, peelers should ring the trunk at base and not break the coil down below the surface of the ground. These sprouts will give rise to "second-growth" poles which are commercially profitable to peel within 25 or 35 years.

(5) Standing trees after being peeled may live on indefinitely, but they never produce a second bark which has any commercial value.

(6) The wood is, for the most part, allowed to rot on the ground. Prompt care would tend to obviate its greatest weakness, checking in seasoning, and it can certainly be applied to some of the uses for which oak wood is prized, and a stupendous annual waste thereby be eliminated.

(7) Forest fires are a source of great annual loss, and coöperative measures should be taken by the State of California, the coast counties, the redwood companies, the tan-bark companies, and cattle-range owners to reduce the danger from fire. A conservative treatment of the redwoods to obtain a continuous crop will be of like advantage to the tan-bark oak mixed with it.

The second section of the pamphlet is by H. T. Betts, on the utilization of the wood of the tan-bark oak, *Quercus densiflora*. He has subjected the wood to a variety of tests, and concludes that it is suitable for most if not all of the uses to which white oak is put. It is as strong as white oak, and much like it in appearance, having strongly marked medullary rays. It requires care in seasoning to avoid warping and cracking, but is not more troublesome in this respect than many eastern hardwoods. It has long been used for wheel-wright work, and a large concern is now making it into flooring, which gives very good satisfaction.

The third section, by C. D. Mell, describes the distribution of tannin in the tan-bark oak. He shows that the twigs have much more tannin than the older wood, so that in extract manufacture it would probably pay to use them along with the bark.

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BOOK NOTICE.

Subject List of Works on Chemical Technology in the Library of the Patent Office, (London).

This pamphlet of 172 pages includes 16 pages devoted to titles of books, articles, and journals relating to leather, covering a wide range both in time and in the topics treated.

ABSTRACTS.

Pollution of Rivers by Tannery Wastes. Paper presented by the Syndicat General des Cuirs et Peaux de France" at the Turin Congress, *Leather,* Oct. 24, 1911.—After stating the nature of the problem and its growing importance, the paper suggests that investigations of methods of purification of tannery wastes should be based on the following points, which are already being considered in a projected law before the French Chambers. *a.* The determination of the physical character of drinkable water: Appearance, odor, color, temperature, mineral or organic matters in suspension. *b.* Chemical investigation of injurious substances in solution. c. Bacterial investigation of the fermentive and putrefactive bacteria. The *Syndicat* recommends that the following measures be taken:—

(1) In each country represented at the International Congress at Turin the appointment of a commission of manufacturers and chemists to study tannery effluents from the point of view of the public health.

(2) The formulation of special appropriate methods of purification for each effluent.

(3) A report by each Commission during the year, giving a resumé of its work.

(4) That the President of the I. A. L. T. C. be asked to put the question on the *agenda* at the next Conference, and that the Conference examine and report upon the work presented.

Mallet Bark. *Leather,* Oct. 12, 1911.—Mallet bark comes from Western Australia, being the bark of *Eucalyptus Occidentalis.* It contains from 45 to 55 per cent. of catechol tannin and leaches easily, yielding very strong liquors. The liquors mellow and sour well, yielding a leather of good weight, good quality, and of a light yellow color.

Oddities in Tanning Agents. H. W. KILLE in *Hide and Leather,* Oct. 21, 1911. A patent dated 1857 describes a process for obtaining tannin from peat by extraction with nitric acid and water. The use of chestnut wood for tanning is said to date from 1863. A decoction of "sweet fern" is mentioned in a patent of about 1866. Another patent involves the use of a solution of potassium carbonate and extract of valonia. A method of treating pig skins preparatory to tanning, patented in 1868,

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calls for the filling of the pores of the skins with a paste made of sugar of lead and rubber solution. In 1880 J. H. Johnson patented the idea of using the bark and root of the pomegranate for tanning. The liquor has little color, so that the leather can be dyed in delicate shades. Another patent describes a tanning solution made of birch bark, blue vitriol, glauber salts, catechu and sulphuric acid. A later method for heavy leather uses tar, turpentine and phenol. Concentrated whey is mentioned as a tanning material in another patent, and bitumen extracted from coal in another.

Carbomethoxy-derivatives of phenolcarboxylic acids and their application in syntheses. (Preparation of crystallized digallic acid.) E. FISCHER and K. FREUEDENBERG, *Annalen*, 1911, 384, 225—244.—The authors have succeeded in obtaining crystallized digallic acid by combining dicarbomethoxygallic acid and tricarbomethoxygalloyl chloride in alkaline solution and hydrolyzing the resulting product. It melts at about 275° (corr. 282° C.), with decomposition, and is much less readily soluble than gallic acid in water; from warm water it crystallizes in fine needles. It dissolves easily in methyl alcohol, less readily in ethyl alcohol and acetone. Diprotocatechuic acid, digentisinic acid, and di-*p*-resorcylic acid were prepared in an analogous manner. All four products (to which the general name "didepsides" is given) give characteristic colorations with ferric chloride solution, and precipitates with solutions of gelatin and of quinine acetate. The use of carbomethoxy-derivatives promises to be of value for the synthesis of tannins.—A. S. in J. S. C. I.

Injury to Kip-leather from Dampness. *Häute und Leder*, Oct. 26, 1911.—It is often observed that when kips are stored for a time they deteriorate. Thus, if 10 bales are bought at the same time, those used at once make good leather, and the proportion of defective hides increases with the time of storing. This seems to be true of a large part of the kips imported from Calcutta. The writer believes that the trouble comes from dampness, the shippers failing to dry the hides properly for the sake of the advantage gained in the greater weight.

L. B.

Carbonic Acid in the Working of Hides. *La Halle aux Cuirs*, Sept. 10, 1911.—Carbon dioxide in solution in water may dissolve lime and carbonate of lime which remains in the hides after washing. This may be done in a wheel, and the writer suggests that a second application of CO_2 under pressure in a drum may be employed to plump the hides preparatory to tannage. Plumping by liquid acids, mineral or organic, consists of an absorption of water, and the increase of volume is due to the fixation of water by the hide, but in the case of carbonic acid the mechanism of swelling is quite different. It does not involve the formation of gelatinous hydrates more or less objectionable, but is simply a mechanical expansion, involving no change in the structure of the hide. No loss of hide substance can occur, and thus a large rendement may be expected.

L. B.

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Injury to Upper Leather by Swelling. *Gerber Courier,* Oct. 14, 1911.—An important mistake in the making of upper leather is the failure to protect the hides from swelling when put into the first liquors. This swelling, due to causes which are largely unknown, causes serious injury to the hides. The hide-fiber is rendered hard, as is seen clearly in the case of sole leather which is purposely plumped in the first liquors, to give it thickness and firmness. Upper leather which is plumped too much is not suitable either for uppers or soles. The main cause of this swelling is a too acid condition of the earlier liquors. Old spruce liquors are specially liable to be too sour, because of their high sugar content. For the same reason, many extracts should be used not at all or only with the greatest care in the manufacture of upper leather. For the first liquor, a mixture of old liquor and new liquor from fresh bark is often very satisfactory. The content both of tannin and acid must be small. L. B.

Estimation of free Sulphuric Acid in White Hide and in Leather. B. KOHNSTEIN, *Collegium,* No. 475, p. 314. The use of sulphuric acid as a plumping agent makes possible its presence in the white hide and in the finished leather, and if the hides are also delimed with sulphuric acid, the quantity in the leather is further increased. Other causes of the presence of this acid in leather are:—the bleaching of leather with lead acetate and sulphuric acid or soda and sulphuric acid; the weighting of leather with barium chloride and the use of an excess of sulphuric acid to convert this into barium sulphate; washing in sulphuric acid in certain dyeing, processes; the drumming of the leather with sulphonated oils, the so-called water-soluble oils. The presence of sulphuric acid in finishing and stuffing materials such as degras and bleached mineral oils may also be mentioned. The blackening of leather with logwood and copperas also contributes some free acid. There is reason to believe that alum tannage releases some sulphuric acid, and it is apt to be present in chrome leather both because of its use in pickling and because it is present in the chroming liquors. Among the common defects due to this acid are brittle grain, rough, loose "cut" of the leather, slight resistance to tearing, the tearing out of stitches in shoes, pocket-books and fancy leather articles, the "spewing" of grease, and light and dark spots on colored leathers.

The removal of sulphuric acid from the leather by repeated washings and neutralization with borax etc. is difficult and at the best incomplete. The same difficulties present themselves to the chemist in his effort to estimate the free sulphuric acid in the finished leather. After having with difficulty extracted the free acid with more or less completeness from the pulverized leather, the solution is so contaminated with other substances that accurate titration with any known indicator is difficult, or impossible. The author used magnesium acid carbonate, that is, a solution of magnesium carbonate in water charged with CO_2, basing his method on the formation of magnesium sulphate by the combination of the free sulphuric acid with the magnesium acid carbonate. Calcium sulphate is

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not transposed by the dissolved magnesium carbonate, the neutralization of the free sulphuric acid taking place without rise of temperature.

The method of examining hide or leather is as follows:—The material is cut into very small shavings, largest dimension not more than 3 mm. About 30 grams of this material is shaken in a separatory funnel with a solution of magnesium carbonate in water charged with CO_2. A stream of CO_2 is passed through the liquid to prevent precipitation of $MgCO_3$. This also promotes the neutralization of the last traces of H_2SO_4 in the interior of the pieces of leather. The liquid is allowed to run into a flask and the operation repeated 3 or 4 times. The flask now contains in solution a quantity of $MgSO_4$ corresponding to the free H_2SO_4 which was in the leather. Before attempting to determine the $MgSO_4$ it is well to boil the solution. This expels the CO_2, and so precipitates most of the $MgCO_3$ which carries down with it much of the tannin, etc. In the case of strongly colored solutions, add 3 grams of freshly ignited MgO and filter. Evaporate an aliquot part of the filtrate and ignite the residue. Magnesium compounds except the sulphate are thus rendered insoluble. The residue is moistened with water containing CO_2 and again gently ignited. The residue consisting almost wholly of $MgCO_3$ and $MgSO_4$ is taken up in distilled water and filtered, the $MgSO_4$ determined in the filtrate and the H_2SO_4 calculated.

The method was tested by carrying through the above process pieces of hide and leather known to contain no free sulphuric acid. No $MgSO_4$ was found in the filtrate at the end of the process. Also materials containing known quantities of H_2SO_4 were examined and found to give closely concordant results. L. B.

The Tannage of Walrus Leather. *Gerber-Courier*, Oct. 28, 1911.—Walrus hides are large and heavy, often weighing when tanned more than 400 pounds. Formerly walrus leather was used for heavy belting, but the price is now so high that they are no longer available for this purpose. The thicker the hide, the more valuable it is. It must be so tanned as not to be hard and compact. Liming should continue two weeks with daily handling. After unhairing and fleshing they are returned to the limes. This destroys the fat which remains and swells the hide very much, an effect which is desired, because it separates the fibers and makes a loose textured leather. The hides are then thoroughly washed in water and are ready for the liquors. Mixed tannage of equal parts valonia, mimosa, myrobalans and hemlock or oak is satisfactory. Walrus leather is used for polishing wheels for cutlery, for pump-leather and other purposes requiring thick, pliable, porous leather. L. B.

Varnished Chrome Leather. *La Halle aux Cuirs*, Oct. 8, 1911.—The writer points out that varnishes suitable for vegetable tanned leather may be unsatisfactory when applied to chrome leather. A varnish must have when dry a coefficient of elasticity equal to or greater than that of the leather to which it is applied. Since chrome leather is more elastic than vegetable tanned, it requires a more elastic varnish. L. B.

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A New Method for Bating Hides and Skins. *Shoe and Leather Reporter,* August 17, 1911.—A recent German patent by Messrs. C. H. Boehringer and Sons, makes use of a solution of lactic acid anhydride in ammonium lactate. This solution contains very little free acid that will immediately be neutralized by the lime in the skins. The process is then one of gradual decomposition of the chemicals, producing free acids from the lactic acid anhydride, which in its turn immediately acts upon the remaining lime in the skins. The method possesses the advantage (it is claimed) that for no long time does free acid exist in the liquor, as immediately the last portion of lime is removed no further decomposition takes place and the action ceases, and there is therefore no danger in having an excess of the bating agent.

The liquor may be prepared by warming 600 grs. of ammonium lactate (commercial 50 per cent.) to 60-70 degrees C., and then adding, with continuous stirring, 300 grs. of lactic acid anhydride (prepared from commercial lactic acid). The stirring is continued until complete solution is obtained.

These figures will give a general idea for the preparation of the liquor; the method is not limited to a definite concentration of the solution.

Lime-Blasting. *Gerber-Courier,* Vol. 52, No. 29.—The author calls attention to the fact that if limed hides are allowed to become partly dry, the lime is converted into carbonate, producing roughness and stained spots, into which the tanning material penetrates but little, so that the spots show in the finished leather. L. A. C.

Formation and Fermentative Destruction of Formic Acid by Yeast: A Contribution to the Knowledge of Alcoholic Fermentation. HARTWIG FRANZEN, Heidelberg, *Zeit. Ange. Chem.*, Vol. 40, p. 194.

According to Wohl's fermentation theory, sugar splits up, giving among the first products, lactic acid which, in turn, decomposes into alcohol and carbon dioxide.

Schade has enlarged this theory, assuming that there is an intermediate step in the decomposition of lactic acid into alcohol and carbon dioxide. Supported by the fact that alpha-oxy-acids split up into aldehyde and formic acid, he believes that lactic acid first decomposes into acetic aldehyde and formic acid, and the formic acid breaks up into hydrogen and carbon dioxide, and that these reduce the acetic aldehyde to ethyl alcohol. Schade, with the assistance of Mr. O. Steppuhn, is experimenting with the behavior of yeasts toward formic acid. For culture medium he used principally clear beer-wort which had been diluted with an equal volume of water and added 1/100 normal quantity of sodium formate. The sterilized flask was sowed with a kind of yeast to be examined, permitted to remain at 27° C and after a certain time the quantity of formic acid estimated.

It was shown that all the kinds of yeast experimented with would bring about a fermentation destroying the formic acid, but if the conditions were modified somewhat, a considerable amount of formic acid

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would be formed and that, side by side, would be found the formation and destruction of formic acid. Through special research it was determined that the surplus of formic acid present had not already existed in the beer-wort at the beginning, that it did not owe its existence to the action caused by the real alcoholic fermentation. The formic acid also forms when sugar decomposes into alcohol and carbon dioxide. It was also further shown that in the fermentation of expressed juices both the formation of formic acid and its destruction by fermentation take place and that the process is connected with the enzymatic action in the cell.

From these researches the author concludes that formic acid is an intermediate product of the true alcoholic fermentation and of the decomposition of sugar into alcohol and carbon dioxide. L. A. C.

Brittle Upper-Leather. *Gerber-Courier*, Vol. 52, No. 36.—Brittle upper leather is not durable, presents a bad appearance when used, and easily cracks when bent. The causes for it may be sought in the preparation of the hides for tanning, in the actual tanning itself, in the dressing or in the finishing.

Sometimes injurious substances are present in the lime or decayed materials are allowed to accumulate in the lime-pits. Corrosive substances like soda, etc., are sometimes added to the lime-pits to hasten the deliming. Sometimes in bating, through poor manipulation the lime is not loosened properly, the washing becomes difficult, lime remains in the de-haired hides and combines with the tanning material forming hard inflexible masses which are inclosed among the fibers of the leather and make it brittle. If limed hides which have not yet been washed or delimed are exposed to the air part of the lime changes into the insoluble carbonate, causing "lime spots" on the hides which are also very brittle. Other substances, such as particles of dirt, etc., may by mechanically choking up the thin outside hide structure, by forming inflexible compounds with the tanning materials or with some other substance, or by a direct injurious action on the hide also contribute to the brittleness of the leather. For this reason bating and washing should be done thoroughly.

The treatment of the hide in the actual tanning also has a great influence on their flexibility and general character. Too much acid in the liquor causes the hides to swell too much and tends to prevent the finished leather from being flexible. An excess of tanning materials shrink it and makes the leather "empty" and "tinny."

The above applies still more to the use of extracts than it does to the use of tan-bark. Because of its rich tannin content, extract works much more intensely than tan-bark and therefore requires care in its use. For upper leather tanning only such extracts are suitable as operate mildly, such as sumac, catechu, gambier, etc. Some others when mixed in the right proportions, give approximately the same results as oak tannage. Among the latter are the pine tan-barks and the quebracho extracts which, at the same time, are classed with the least expensive

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tanning materials. Brittleness may also be caused by the insufficient washing of the leather after the tanning. Because of this the hides come in a hard state to the finishing table and often liquor, extract, and free tanning material remains on them. This hardens the leather and chokes up the grain so that hardness and brittleness are sure to result. Upper leather, especially extract tanned, should therefore be washed thoroughly, be given a good rubbing, and then be worked with the slicker.

A grease which is too hard does not penetrate into the leather but fastens itself on the outside, making it dark and ugly. A grease which is too thin penetrates through the leather, gives it no firmness or strength, and makes it flat and limp. This blemish also appears if the leather, when greased, is too wet or too dry, or if the greased leather is dried at too high or too low a temperature, or if the leather is rolled too wet. L. A. C.

A Modification of the Kjeldahl Apparatus for the Estimation of Nitrogen. DR. ING. KREIGER, *Chem. Zeit.*, 1911, p. 1063.

As the chief source of error in the Kjeldahl nitrogen method lies in the neutralization with NaOH and the subsequent distillation, an improvement is proposed to prevent the escape of NH_3. Muller (*Chem. Zeit.* 1910, page 1308) and Block (*Chem. Zeit.* 1911, page 208) fused on the top of the distillation flask a small dropping funnel, through which the NaOH should flow into the flask. A much simpler apparatus is made by inserting a dropping funnel through a double-holed stopper to the bottom of the flask.

Another source of error arises from the "bumping" of the liquid in the flask as the solution becomes concentrated. This inconvenience can be met by replacing the water lost by evaporation so that the concentration of the liquid does not vary, or so large a quantity may be put in at first that the liquid will not "bump" during the distillation of the necessary quantity. The gradual replacement of the evaporated water may be accomplished by passing a current of steam through the apparatus. The tube through which the steam is introduced may afterwards be used to convey a current of ammonia-free air in order to sweep out the last traces of ammonia from the apparatus. L. A. C.

The Connection between Tannin and another Colloid in Ripe Fruits, particularly the Persimmon. FRANCIS E. LLOYD, *Alabama Polytechnic Institute, Koll. Zeit.*, Vol. IX, No. 2, pp. 65-73.

Several different investigations have established the fact that the 2 or 3 per cent. of tannin which an unripe persimmon contains seems to disappear when the fruit is ripe—at least it can no longer be distinguished by taste. There are many opinions about this process. Some think that the tannin is absorbed by certain cells in the pulp which hold it insoluble—others that it joins pulpless cells, takes on a jelly-like form and becomes insoluble; and others, (W. D. Bigelow, H. C. Gore and B. J.

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Howard, Jour. Am. Chem. Soc., 28: 688-703) hold that this tannin in ripe fruits is extractable by means of weak mineral acids—but they have been unable to determine the nature of the pulp from which they get it.

The author purposes to show that in certain tannin cells, particularly in some fruits, there is, besides the tannin, another colloid whose special function it is to absorb tannin during the ripening of the fruit, to hold it fast and thereby render it inextractable. This colloid complex would be a stable colorless solution giving the tannin color reaction.

The tannin cells occur in certain sections of the unripe fruit and can be clearly distinguished in a section under water viewed through the microscope. This is because the second colloid is absorbent and the water it takes up bursts the cell wall and lets the tannin out. It can be seen flowing through holes and diffusing. But when the fruit is ripe, although the second colloid still takes up enough water to burst the cell wall, it does not dissolve as readily if at all, and very little tannin comes out.

The structure of the "tannin mass" or jelly-like substance is remarkable. The tannin fills the large vacuole and is penetrated by different tiny canals. Besides the large vacuoles there are others which contain no tannin. But the jelly-like mass in the tannin cells takes up the tannin and holds it. The jelly mass grows stiffer as the tannin is absorbed and becomes colorless. In this condition it can be preserved in water for a long time.

This colloid complex may be an albuminoid or a carbohydrate. The author holds that it is the latter. When a solution of the tannin cells was treated with 50 per cent. nitric acid and then with 1.25 per cent. lye, and then with Fehling's solution it gave sugar, *i.e.*, this colloid hydrolizes into sugar, and is therefore a carbohydrate. E. A. B.

Wood Pulp and Tanning Extracts. HUGH GARNER BENNETT *in Shoe and Leather Reporter*, Oct. 19, 1911.—In the first place it may be asked. "Is it a tanning material in the same sense as quebracho, chestnut, oakwood, etc? Does it contain any substance which may be classed among the tannins?"

The answer to this must certainly be negative. Although the term "tanning," may not include the treatment of hides with mineral salts, oils, fats, aldehydes, etc., the term "tannin" is restricted to those substances obtained by extracting certain vegetable matters with water. These bodies (tannins) are chemical individuals which are very closely allied in the chemical sense, and belong to the same family of chemical compounds. They all contain only carbon, hydrogen and oxygen, they belong to the aromatic division of organic compounds, and they are derivatives either of catechol or of pyrogallol. Even their very dilute solutions will give a precipitate with a 1 per cent. gelatin, 10 per cent. salt solution. They are precipitated more or less completely by solutions of many metallic salts, alkaloids and basic coloring matters. They are unstable in the presence of alkalies, and yield characteristic colors with solutions of ferric salts, and with potassium ferricyanide and ammonia.

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They can be oxidized in acid solution by permanganate of potash, of which a definite and characteristic quantity is consumed in each case under appropriate conditions. This description or definition may be applied without exception to every vegetable tanning material hitherto used commercially.

Now the wood pulp extracts referred to do not contain tannin in this sense. It is true that they contain certain colloidal matters which hide powder will remove from solution, as in the ordinary process of analysis, but that could also be said of many other substances that are not tannins, *e.g.*, gallic acid. These so-called pine wood extracts and spruce extracts, are therefore not tanning extracts in the proper and usual sense of the word, but are strong solutions of mixed vegetable matter of a ligneous nature which answer *some* of the tests for tannin. They do not contain those long familiar astringent bodies which from time immemorial have converted pelt into leather.

"How May these Extracts be Distinguished from a Genuine Tanning Extract?"

This may easily be ascertained by applying certain tests for tannin which are well known and reliable. A few may be cited here, perhaps, with advantage. It is assumed that a solution of the extract is made up of the same strength as for analysis, *i.e.*, containing 0.4 per cent. of apparent tan.

An infusion of any vegetable tanning material, containing even 1 part of tannin in 10,000 will give a precipitate with gelatine and salt. The pure wood pulp extract gives no precipitate with this reagent, and therefore contains no tannin.

2. The official hide powder method of analysis, and the Lowenthal method which depends upon a different principle, viz., the oxidation of the tannin by potassium permanganate, will give results in fair agreement when operated as described by Procter & Hirst (Journ. Soc. Chem. Ind., 1909, March 31st). In the case of these wood pulp extracts, however, this is not the case. An extract showing 25 per cent. apparent tan by the hide powder process will only show about 4 per cent. tan by the Lowenthal process.

3. These wood pulp extracts, containing ligneous matters, answer the following test for lignin as modified by Procter and Hirst. To 5 cc. of the extract solution, 0.5 cc. of aniline is added and the whole is well shaken, and 2 cc. of concentrated hydrochloric acid is then added to the mixture. With all ordinary tanning extracts this addition of acid has the effect of immediately clearing the turbidity caused by the aniline and a perfectly transparent solution results, but with pure wood extract or where pine wood extract is present, even in comparatively small quantity, a precipitate is rapidly produced which rises gradually to the top of the liquid. A very slight turbidity occasionally is obtained with pure tanning extracts, due to the presence of small quantities of ligneous matter.

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4. Practically all the vegetable tanning materials give a precipitate with a 4 per cent. solution of tartar emetic. Wood pulp extract gives neither precipitate nor turbidity. (*Collegium*, 1911, 331.)

5. If a solution of the extract (50 cc.) be boiled with 25 cc. of a solution containing 100 cc. water, 150 cc. formaldehyde (40 per cent.) and 100 cc. conc. hydrochloric acid, using a reflux condenser, all catechol tannins would be precipitated, whereas wood pulp extract yields no precipitate; and if a little ferric alum and sodium acetate be added all pyrogallol tannins would yield a violet color, whereas pine wood extract yields none.

"How Might the Presence of this Material be Ascertained if Mixed with an Ordinary Tanning Extract?"

If some true tannin extract be incorporated with wood pulp extract it may be made to answer all the qualitative tests for tannin. As this material is not a true tanning material its detection as an adulterant is a matter of considerable practical importance to the tanner, and considerable attention has been given by Prof. Procter, Hirst, Stiasny, Wilkinson and other workers to this question. Their results and conclusions, which are somewhat isolated and scattered, may be summarized as follows:

(a) The aniline test recorded above may be used to detect any appreciable quantity of wood pulp extract in admixture with other extracts.

(b) Analysis by both hide powder and Lowenthal methods if in considerable disagreement, show the presence of pine wood extracts as an adulterant.

(c) Wood pulp extracts contain small quantities of manganese and aluminum salts, which form precipitates with tannins when heated with an electrolyte. Hence to 5 cc. extract solution add 10 cc. 10 per cent. sodium acetate solution and heat. If no precipitate is obtained the absence of wood pulp may be concluded. This, however, is only a negative test, the appearance of a precipitate does not signify with certainty the presence of wood pulp in the extract. See *Collegium* 1908, 348, 307, or *Journ. Soc. Chem. Ind*, 1908; 1030, for further details.

(d) If a solution be made 6 to 8 times the ordinary strength, 5 cc. together with 10 cc. of 40 per cent. ammonium acetate solution gives a clear solution with all catechol tannins, *i.e.*, quebrachos, mangrove, ulmo, hemlock, gambier, pistacia, mimosa, etc., but if wood pulp be present a copious precipitate is produced. Curiously enough wood pulp extract alone gives no precipitate. As many of the pyrogallol tannins give a precipitate their absence is necessary for this test. The *Collegium* 1911, 322, for further details.

(e) Another test particularly useful for detecting adulteration in chestnut and oakwood extracts, is that of Stiasny and Wilkinson (*Collegium*, 1911, 320). To 5 cc. extract solution of ordinary analytical strength, 5 cc. of 10 per cent. lead acetate are added, and a portion of the clear filtrate

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mixed with an excess of 15 per cent. caustic soda solution. If the solution remains colorless no wood pulp is present; 10-20 per cent. wood pulp give a distinct yellow color. In the cases of quebracho, sumach and pistacia the test must be carried out with basic lead acetate and is less delicate.

Will Wood Pulp Extracts Make Leather?

It is pointed out that although these extracts may not contain any true tannin, still they contain matter which is absorbed by hide powder in analyses, and which is absorbed by hide or skin pelt. It is claimed therefore that such extracts, whatever chemical tests they may answer or not answer, are tanning materials, and may be used as such. This may be true, but it may be necessary to use them in a very different way and to take very different precautions. It would be interesting, perhaps, to quote the words of Professor Procter on this question: "If attempts are made to tan with this extract alone, it is difficult, if not impossible, to obtain a product which deserves the name of leather, the surface being apparently tanned while the interior remains raw and unaltered, and the hide dries horny and usually of unsatisfactory color. If, however, the hide be in the first instance partially tanned with some ordinary tanning material, or if some other tanning extract be used in conjunction, leathers are produced similar in appearance to those of ordinary tannages."

Cellulose Extract. W. EITNER, *Gerber*, 1911 (37) 227-9, 241-3, 255-6. —As a cheaper domestic substitute for the foreign tans rendered still more expensive by useless duties, the residual lye from the cellulose factories has attracted attention for some time. In the Mitscherlich wood pulp process, wood is treated with Ca or Mg sulphite under pressure and the substances encrusting the cellulose fiber brought into solution. Although the original pine or fir wood contains no tannin, it was proposed (first by Mitscherlich) to employ the lye for tanning. Ziegler next patented a process following a chrome tannage; this was shown to merely dye and fill the tanned hide and the process did not come into use as the leather was miscolored and altered on storage. The fact that this extensive by-product was a nuisance and expensive to burn, stimulated the attempt to overcome the objectionable color given to leather and to remove the SO_3 and earthy salts. Prof. König in Brünn devised a successful process for decolorizing with Zn dust and precipitating the lime salts. The product, pine wood extract, found acceptance as a filling material, especially abroad. Although König's process does not convert the organic material into tanning agents, the small amount of zinc sulphate retained imparts a slight tanning effect. This Zn content may be used in analysis to detect adulteration with pine wood extract.

Recently a brand of pine wood extract named "Excelsior," manufactured in Germany, has been put upon the market, for which extravagant claims are made. Basing on a Frieberg analysis (filter method), the circular claims:

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	Per cent.
Tanning substance	25.8
Soluble non-tans	28.0
Insoluble	0.0
Water	46.2

Further, it is maintained that by oxidation during acid formation, the greater part of the non-tans are converted into tanning substances, hence the preparation contains about 50 per cent useful tans.

The author has never found real tanning material in cellulose extract. According to his analysis, the new German extract is of about the same composition as the Hungarian pine wood extract made by the König process:

	German ext.	Hungarian ext.
Substances absorbable by hide powder	22.59	22.82
Substances not absorbable by hide powder	28.19	27.54
Insoluble	0.0	0.0
Water	49.04	49.64
Ash	7.50	5.32

The circular further claims that Excelsior extract has high swelling power, being rich in sugar formers. This does not harmonize with the previous statement that the extractive substances change to tannin, neither are sugar or acid forming substances present. Otherwise this by-product has been chemically utilized long ago. Pine bark extract contains saccharine bodies, but this does not apply to products from the wood. It is also claimed that Excelsior extract renders quebracho completely soluble. By experiment, the author found that crude cellulose lye dissolved some 3 per cent., its weight of sediment from Argentine quebracho, the difficult soluble part being dissolved; the remainder remained insoluble. Neutralized and purified cellulose lye had little solvent action. It may be said of the two market brands of pine wood extract, that they promote the solubility of quebracho merely to the same extent as chestnut or oak extracts.

After a caustic review of an Excelsior "catechism," the writer quotes the results of experiments upon the tanning effect of cellulose extract. White hide was treated with a liquor of 25° barkometer which fell to 15° in one day. The liquor was then strengthened from time to time until no further weakening resulted, finishing at 55° in one month. After drying, the leather was horny and stiff and on boiling went entirely to glue, showing no tannage had taken place. Another experiment showed that after washing there was a gain only of 0.55 per cent. due doubtless to dyes. For another series of tannages with (I) German pine wood extract, (II) same, mixed with quebracho extract, (III) quebracho alone, rendements were obtained:

	I	II	III
After bleaching, unwashed	38	69	65
After soaking in water 2 days	32.3	58.5	59.3

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This shows that the sulphite extract neither alone nor in mixture with quebracho, had any tanning effect. A saving of time equal to 25 per cent. resulted from using mixture (II) as compared with (III), due doubtless to influence on speed of diffusion.

As a filling material in currying leather already tanned, cellulose extract is very efficient, because of its penetrating power. In drum tanned leather, a gain of 8.5 per cent. was easily reached by the writer. Excess must be avoided however, else the leather becomes hard and brittle. In dressing sole leather, 12-15 per cent. was easily incorporated; the leather becomes dark however, and it is difficult to avoid spots in bleaching.

In conclusion, the writer quotes reports from practical tanners showing disappointing experiences with cellulose extract. This material is already extensively used in blending special mixtures and as an adulterant.

W. J. K.

The Analysis of Chrome Leather, III. GEORG GRASSER. *Collegium*, 1911, 365-6. Fahrion's last article, (abstr. ant. p. 498) is criticised. In his published process only the determination of H_2SO_4 (including sulphates!) is described (acidification with HCl!) and the sulphate resulting from deacidifying with borax is included with the H_2SO_4. Neither does Fahrion state how the absence of HCl is proven. The author again emphasizes that indicator tests for free acid in leather sections are unreliable. As to the saponifiable matter in hide itself, the author has made blank experiments upon hide powder and found that errors from this source are negligible, especially in technical work; moreover chrome tanned hide would scarcely yield a trace of basic (sic) substance.

The author does not claim absolute precision for his own method (abstr. this JOURNAL 5, 528) but that it is better suited as a rapid method for technical work. The following results were obtained in the factory:

One-hundred gms. de-acidified chrome leather (dry) gave 0.902, 0.927, 0.853, 0.645 gms. acid reckoned as H_2SO_4; 100 gms. not de-acidified leather gave 1.815, 1.802, 1.695, 1.530 gms. acid as H_2SO_4. W. J. K.

Analysis of Chrome Leather, IV. W. FAHRION. *Collegium* 1911, 366-8. —Replying to the above, the author declares that Grasser has not understood him. He does not claim to determine free acid in leather, but the total acids and chromic oxide and draws conclusions from the ratio of the two. In his own analyses, HCl was known to be absent, hence HCl was used for acidulating. If HCl were present, two analyses could be made, acidulating with HCl and H_2SO_4 respectively, or the alkaline solution could be analyzed in aliquot parts, all ordinary procedures in analysis. The assertion that sulphates from borax neutralization are included is found unintelligible, since practically all this goes to the bath. Grasser's own figures demonstrate the formation of acid (glycocoll) from hide substance. The free acid, 0.9 per cent. would not be tolerated if really H_2SO_4, by consumers. De-acidified chrome leather certainly contains less acid than sufficient to fix the Cr_2O_3. Even if Grasser's method

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be used only to ascertain differences, before and after de-acidifying, these would only apply to the one manufacture, for chrome leather may vary from 3 to 6 per cent. Cr_2O_3, involving a like variation in the acid.

The author agrees with Grasser that various ratios of base, according to circumstances, may give the maximum tannage. It is desirable that statistical analyses of good leathers be made to ascertain the limits, and this was the object of his original paper. W. J. K.

Dyeing Experiments with Coal Tar Colors. GEORG GRASSER. *Collegium*, 1911. 379-82.—These dyes may be classed in three groups. (1) Substantive dyes which dye unmordanted leather in neutral or alkaline baths. (2) Acid dyes, same, in acid baths. (3) Basic dyes, which dye mordanted leather in neutral to weak acid baths. In mordanting leather, tannin is exclusively used; sumac or gambier as well as logwood in blacks, are the materials.

The author has found chrome leather skivings a good material for testing dyes. The moist skivings direct from the machine are de-acidified by shaking half hour with a half per cent. borax solution at 30° C, then washed and finally air dried. For basic dyes, the washed shavings may be treated with sumac before drying. Also if black tests are to be often made, a stock of material may be likewise prepared with logwood. Besides economy of labor, this item insures all tests being made on one uniform material. The color tests are made by treating on the water-bath at 60-90° C., with solutions containing 0.4 to 0.8 per cent. of dye. For qualitative tests, 0.6 to 0.9 per cent. solutions are used; 10 gms. skivings generally suffice to exhaust the dye from 100 cc. liquor, especially at the higher temperatures. If the last traces of dye (generally valueless however) are not withdrawn, the amount remaining may be estimated by a colorimetric comparison. W. J. K.

The Employment of Chrome Leather for the Valuation of Tannin Extracts. GEORG GRASSER. *Collegium*, 1911, 390-2.—The tintometer has not proved successful in valuing the coloring power of extracts for practice. Pelt is too variable in character to give uniform results and it is necessary to remove the lime by acids which in their turn modify the color. Gansser's animalized cotton (ante. p. 165) is important but the apparatus required is too expensive except for extract factories.

The writer has obtained good results as follows: 25 gms. liquid extract (8 gms. solid) are dissolved in 100 cc. H_2O at 70°, cooled and shaken one hour with a piece of chromed calf leather, 8 by 10 cm. This is left lie in the dark 3 hours. Then well washed, pressed and air dried. A good color is obtained, not the least affected by the original chrome green as proven by blank tests.

The rational way to comparatively estimate the coloring effect of extracts is not as usual, to take equal amounts, but equivalent amounts, according to the tannin content. For example, to compare two chestnut

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extracts of 24 and 30 per cent. tannin, 25 and 20 gms. of each respectively should be employed. One of the chief defects of the hide powder method of analysis, consists in the removal of more material from the solution than is done in actual tannage, as shown by the relative decolorization. This also applies in judging extracts, hence the author proposes to take account of the relative tannin content in testing as prescribed above.

W. J. K.

New Studies on the Tannage of Gelatine and Hide; Application in Preservation of Hides. L. MEUNIER AND A. SEYEWETZ. *Collegium,* 1911, 373-9. —A preliminary notice has already appeared (abstract, ante, p. 528) relating to the action of bromine and hypobromites on gelatine and hide. The authors now include chlorine and iodine and define the conditions of tannage by halogens.

Gelatine.—All experiments were made by subjecting 10 gms. finely flaked gelatine to the action of 500 cc. of the reagent and testing a sample with boiling water every ¼ hour. Gaseous chlorine was found to decompose gelatine but not to insolubilize it. Chlorine water at 15-20° effected no insolubilization for the hydrolysis of the gelatine by the HCl present prevented this. The addition of salt however, and low temperatures retarded the hydrolysis; the best results were obtained with 50 gms. salt in the vicinity of 0°. Hypochlorite of soda readily insolubilized below 10-12°, a small addition of HCl reducing the time of complete insolubilization one half; at higher temperatures swelling results and the action is incomplete. Chloride of lime gave similar results in the neighborhood of 0° and also practically good results at 10-12°. Raising the temperature decomposed the gelatine more rapidly than with the Na salts. After thorough washing and removing the excess of free chlorine with sodium bisulphite, the dried products yielded the following percentages of chlorine:

Insoluble gelatine from Na hypochlorite	0.23	0.26	0.29	
Insoluble gelatine from Ca hypochlorite	0.38	0.32		

Bromine water acts more regularly than chlorine, the formation of acid being slower. The swelling effect of the HBr may be prevented by addition of 100 gms. salt; favorable temperature, 10-12°. Hypobromite of soda gave good results. The purified dried products gave percentages of bromine:

Insoluble gelatine from bromine water ..	0.89	0.92	0.88	0.86
Insoluble gelatine from NaOBr.	0.90	0.95	0.89	..

Iodine and hypoiodides gave no insolubilization.

Hide. The action of halogens upon hide is a form of tannage, bromine being the most energetic. The product is less resistant to boiling waters than quinoned hide and resembles pelt.

Applications. For preserving white pelt, the methods of desiccation, liming and pickling, each have their disadvantages. The authors made preliminary experiments in treating 100 kg. pelt with 300 liters water

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containing 3 kg. chloride of lime, 3 kg. salt, with good results. The use of chlorine for a foretannage is being studied.

W. J. K.

PATENTS.

Apparatus for Desiccating and Collecting Solids from Fluid Substances U. S. Patent No. 1,007,381. WILLIAM S. OSBORNE, New York, N. Y., Assignor to Osborne Desiccating Machinery Company.

Leather-glazing Machine. U. S. Patent No. 1,007,160. WILLIAM B. TURNER, Boston, Mass., assignor to Leather Finishing Co.

Leather-conveying Mechanism. U. S. Patent No. 1,007,841. CLARENCE U. BEADENKOPF, Wilmington, Del.

This device is apparently intended to convey leather through a drying room.

Leather; Artificial. Eng. Pat. No. 15,761, July 6, 1911. E. REIDEL, Mannheim, Germany.

Animal fibers, prepared from tendons, sinews, and waste products by drying, pressing and shredding, are interwoven with filaments of hemp, tow, flax, jute, etc., into a mat. The mat is immersed in solutions of acids or alkalies to swell the fibers, pressed into a solid piece and subjected to the action of a tanning liquor and finally dried. Before the pressing, blood, globulin, or fibrin is incorporated with the material to make it of a firmer texture, and the flexibility is increased by addition of soap solution or an emulsion of ceresin or paraffin.

J. R. B. in J. S. C. I.

Glue and the like; Manufacture of——. Eng. Pat. No. 12,566, May 24, 1911. Under Int. Conv., Jan. 17, 1911. CONWAY, BARON VON GIRSEWALD, Berlin.

The crude materials from which the glue is made, viz., bones, are subjected for a relatively short time to the action of steam at a comparatively high pressure, and afterwards by suddenly reducing the pressure to below that of the atmosphere and simultaneously admitting small quantities of steam, the temperature is caused to fall rapidly, so that injury to the glue is minimized. The action is more intense but shorter, and the product is of a finer quality than that obtained by long heating. Steam at a pressure of two and a half atmospheres is used at the outset of the operation, but for a period of only 10—15 minutes. The steam which is admitted into the chamber supplies the water required for the formation of the glue solution.

J. R. B. in J. S. C. I.

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